VOL. XVI. SEPTEMBER, 1894. NO. 9.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

AN ATTEMPT TO PREPARE MOLYBDENUM HEXACHLORIDE.

BY EDGAR F. SMITH AND HENRY C. BURR.

Received June 15, 1894.

IT is well known that Teclu[1] obtained the hexachloride of tungsten by acting upon the trioxide of the metal with phosphorus pentachloride. The treatment of molybdenum trioxide in the same manner gave in one instance the compound $MoCl_5.POCl_3$ and in another, $MoCl_5.PCl_5$. In both of these derivatives the pentachloride of the metal is present. It would, therefore, seem that the metal is incapable of carrying the sixth chlorine atom. Reuter[2] heated both the trioxide of tungsten and that of molybdenum with silicon tetrachloride; his products, however, were not hexachlorides. Passing by his observations it was thought that if a partially chlorinated molybdic acid were exposed to chlorinating agents the residual oxygen might be removed and that then perhaps the hexachloride would be present in the reaction product. To this end molybdenyl chloride, MoO_2Cl_2, was mixed with an equivalent quantity of phosphorus pentachloride and heated in a sealed tube in the presence of chlorine to a temperature of about 170° C. On cooling, it was found that the tube contained a mass of greenish-black crystals, which when carefully freed from adherent phosphorus oxychloride by distillation in an atmosphere of chlorine gave a product that on analysis yielded figures approximating the pentachloride more closely than the hexachloride.

Silicon tetrachloride was substituted for the phosphorus pentachloride and the experiment repeated. The resulting crystalline

[1] *Ann. Chem.*, (Liebig's), **187**, 253.

[2] Dissertation, Tübingen, *1893*.

8-3-94

product was quickly removed to a boat and carefully distilled in an atmosphere of carbon dioxide. Brown vapors were expelled from the boat, which finally contained nothing but white silica. The brown vapors quickly condensed in the colder portion of the tube, and upon analysis gave results varying between those required by the tetrachloride and pentachloride.

The conclusion to be drawn from these experiments then is that notwithstanding the molybdenum atom has already been partially chlorinated, and apparently is in a suitable condition to pass into the hexachloride, it yet does not do so, and we can hence only say that the molybdenum is either not sexivalent towards chlorine, or that at the elevated temperature at which these reactions took place, the hexachloride, if formed, cannot exist, but is dissociated into lower chlorinated derivatives.

On heating pure, finely divided molybdenum, intimately mixed with sugar-carbon, in an atmosphere of chlorine the invariable product was the pentachloride.

The temperature doubtless exerts a great influence in these reactions.

It has been observed in this laboratory that when metallic molybdenum acts upon an aqueous solution of ferric chloride rapid reduction of the ferric salt ensues with accompanying solution of the molybdenum. From a careful determination of the amount of iron thus reduced, the molybdenum evidently dissolves as a hexad, and it may be that if such solutions were allowed to evaporate slowly in desiccators, the hexachloride or some double salt, formed from it and ferrous chloride, might be found. Search will be made in this direction.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

THE ACTION OF HYDROCHLORIC ACID GAS UPON SODIUM VANADATE.

BY EDGAR F. SMITH AND JOS. G. HIBBS.

Received June 18, 1894.

THE reaction of Debray[1]—the volatilization of molybdic acid by means of hydrochloric acid gas,—has suggested a number of experiments which of late have been tried in various

[1] *Compt. rend.*, 46, 1098.

directions in this laboratory. Among others we have exposed sodium pyrovanadate to the influence of the gas at temperatures ranging from the ordinary to about 440° C., and have found that it is possible in this manner to eliminate the vanadic acid from its salts.

In several experiments we used a preparation from Merck, marked "sodium vanadate." It was not white in color, but showed here and there spots that were yellow to reddish-brown. Weighed portions of this salt, after complete drying, were exposed in boats, to the action of pure hydrochloric acid gas. As soon as the boats were introduced into the gas the salt, *in the cold*, acquired a red-brown color. On the application of a gentle heat, vapors of similar color appeared over the boat and condensed in the colder, anterior portion of the combustion tube to a reddish-brown, semi-transparent, oily liquid, which was taken up by water with a brown color. In the boat remained sodium chloride, containing here and there minute black spots. On dissolving the salt, the black insoluble material was carefully examined and proved to be traces of vanadic oxide. They were undoubtedly present in the original salt and were the real cause of the reddish color noted in it. That they were not volatilized may be due possibly to the fact that they had previously undergone strong ignition, and were hence less volatile, although it was observed that by continued heating of the salt, while yet exposed to hydrochloric acid vapor, they gradually grew less in quantity. The results obtained in the four experiments, which follow, while they do not agree with the theoretical requirements yet show that the source of error was constant.

1. 0.0795 gram sodium vanadate gave 0.0546 gram sodium chloride, whereas if the salt analyzed had been pure sodium pyrovanadate it should have given 0.0606 gram sodium chloride.

2. 0.0786 gram sodium vanadate gave 0.0535 gram sodium chloride, instead of 0.0599 gram.

3. 0.1006 gram vanadate gave 0.0683 gram sodium chloride, instead of 0.0767 gram.

4. 0.1322 gram vanadate gave 0.0916 gram sodium chloride, while theory required 0.1007 gram.

Taking the purest vanadic acid that we could find, pyrovana-

date of sodium was prepared and obtained pure after several recrystallizations. The anhydrous material was exposed to hydrochloric acid gas as before with results that indicate a quantitative separation of the acid.

1. 0.1240 gram sodium pyrovanadate heated to 440° in hydrochloric acid gas gave 0.0935 gram of salt instead of 0.0945 gram.

2. 0.2197 gram sodium pyrovanadate gave 0.1669 gram sodium chloride, while theory requires 0.1672 gram.

The sodium chloride from these last two experiments was perfectly white in color, soluble without residue in water, and on examination showed no evidence of the presence of vanadium. The volatile product had the appearance of the compound $2VO_2.3H_2O.4HCl$ obtained by Berzelius when acting on vanadic acid with concentrated hydrochloric acid. If such be really the case we may suppose that in our reaction changes occurred similar to those indicated in the following equations:

$$\text{I. } Na_4V_2O_7 + 4HCl = 4NaCl + V_2O_5.2H_2O,$$

$$\text{II. } V_2O_5.2H_2O + 6HCl = 2VO_2.3H_2O.4HCl + Cl_2.$$

It will, however, be necessary to subject this volatile product to careful analysis before making a positive assertion in regard to its composition.

It is our intention to pursue this study further with the view of ascertaining whether by means of this reaction it will be possible to separate vanadic acid from certain of its associates from which it is now removed with difficulty. From the ease with which the transposition occurs we may hope that the atomic mass of vanadium may be determined after the same fashion as was done in the case of molybdenum.[1]

UNIVERSITY OF PENNSYLVANIA.

June, 1894.

ON SOME OF THE ARSENIC TESTS OF THE U. S. PHARMACOPOEIA (1890).[2]

BY CHARLES O. CURTMAN.

Received June 15, 1894.

NOTE.—In applying Bettendorf's test for arsenic, the Pharmacopoeia directs that to a small quantity of the liquid to be tested, which should contain much hydrochloric acid, or should be a solution of the substance

[1] *Ztschr. anorg. Chem.*, 5, 280.

[2] Report of the Pharmacopoeial Research Committee B.

to be tested in pure, concentrated hydrochloric acid, there should be added an equal volume of a saturated solution of freshly prepared stannous chloride in pure, concentrated hydrochloric acid, *together with a small piece of pure tin-foil.* The presence of arsenic is revealed by the production of a brown color or brown precipitate, the appearance of which is hastened by a gentle heat. By an oversight, the direction to add the tin-foil was inserted or left standing in the tests for arsenic in bismuth or antimony salts, in which it leads to false conclusion, as the following paper will show. (Dr. Chas. Rice, Chairman U. S. P. Revision.)

A NUMBER of experiments have been made for the purpose of ascertaining the conditions most favorable to the result of the test for arsenic by stannous chloride (Bettendorf's test and its modifications).

The inquiry was directed to the following points:

1. The limit of sensitiveness of the test in its various modifications.

2. The best proportion of reagent to specimen.

3. The influence of the use of metallic tin together with the stannous chloride.

4. The influence of the presence of other substances in the specimen tested.

I. Limit of Sensitiveness.

The following reagents were used:

a. The solution directed for Bettendorf's test by the U. S. P., consisting of a saturated solution of pure stannous chloride in pure, concentrated hydrochloric acid. The specific gravity of this solution was 1.407.

b. Metallic tin, perfectly pure, in thin cylinders, from which shavings of about 0.1 gram were taken as needed.

c. Stannous chloride solution prepared according to the German "Arzneibuch," by saturating a mixture of five parts of crystals of stannous chloride and one part of hydrochloric acid with dry hydrochloric acid gas. The specific gravity = 1.912.

All of the materials used were previously tested for absence of arsenic by Gutzeit's test, so as to exclude any fallacies arising from the introduction of even small traces of arsenic by the reagent, which might cumulate with those in the specimen.

It was easy enough to procure pure metallic tin, but impossible to obtain, from local dealers, hydrochloric acid sufficiently

free from arsenic to stand Gutzeit's test for one hour. So that I had to distill from purified sulphuric acid and pure sodium chloride the hydrochloric acid required for the preparation of the reagents.

A number of specimens of arsenic solution were made, containing free trioxide, sodium metarsenite and sodium arsenate in such proportion that each set corresponded exactly to an equal amount of As. They were:

Arsenic trioxide ($As_2O_3 = 197.68$), of which 1.31962 grams contain one gram of As.

Sodium metarsenite, ($NaAsO_2 = 129.82$), of which 1.7332 grams contain one gram of As.

Sodium arsenate, U. S. P. ($Na_2HAsO_4 + 7H_2O = 311.46$), of which 4.51834 grams contain one gram of As.

The solutions used for experiment contained from 0.5 gram to 0.01 gram of As. Of these, one cc. was used for each trial and the amount of reagent mixed with this varied from one cc. to three cc., so as to correspond with the limits prescribed in the pharmacopoeial tests. When metallic tin was added to the reagent, one cc. each of the specimen and the stannous chloride solution was used. In some cases of doubt a ten-fold quantity (10 : 30 cc. etc.) was used to obtain sufficient material for colorimetric comparison.

A uniform application of heat was effected whenever needed by imbedding the series of test-tubes under observation, to an equal depth, in a sand-bath heated to about 80° C.

Whenever comparisons of color became necessary to decide whether a deeper color had been produced than that of the unaffected reagent (as was especially necessary with the yellowish solution of the German pharmacopoeia), or whether a greater or less intensity of color characterized the reaction, narrow graduated cylinders of ten cc. capacity, were used in a dark box with light reflected from beneath, or occasionally for still greater accuracy, a pair of Hehner's colorimeter cylinders of 100 cc. capacity, also placed for observation into a dark box, admitting from beneath light reflected upward by a plate of milk-glass placed at an angle of 45°. With the aid of these appliances the following results were obtained:

a. With the U. S. P. solution of stannous chloride of sp. gr. 1.467, one cc. of each of the three specimens, containing 0.5 mgm. of As, was mixed in the different proportions stated below, and kept at ordinary temperature for one hour.

With one cc. of reagent a sharp reaction had taken place at the end of the hour. With two cc. of reagent the reaction was obtained earlier and was more intense at the end of one hour. With three cc. of the reagent the reaction was still more speedy, and at the end of the hour more intense.

No difference could be noticed either in time or in intensity between arsenic in the state of trioxide or pentoxide.

When the test-tubes were arranged exactly as before, but placed in hot sand, the time was somewhat shortened, and a slight increase of intensity noticed in all of the specimens.

b. When one cc. of the U. S. P. solution was used with one cc. of solutions containing 0.5 mgm. of As, and a small piece of metallic tin added and heat applied, the reaction was almost instantaneous, and in three minutes a very sharp, unmistakable coloration appeared which continued to increase in intensity for about ten or fifteen minutes, but was not notably darker at the end of the hour. No difference appeared in the different solutions containing arsenite and arsenate.

c. When from one to three cc. of the stannous chloride of the German pharmacopeia was used with one cc. of the solutions containing 0.5 mgm. of As, there was a slight darkening of the color in a few minutes, which continued to increase to the end of the hour. No difference was perceivable between the arsenous and the arsenic preparations. At fifteen minutes the specimens treated by the U. S. P. solution and metallic tin showed a much greater intensity of color, but toward the end of the hour there was but little difference perceptible between the color of the specimens treated with three cc. of the German reagent without heat, and that treated with one cc. of the U. S. P. reagent, metallic tin, and heat. The specimens containing less than 2.5 cc. of reagent showed a less intense color.

These experiments were repeated with the three solutions containing 0.05 mgm. of As. in one cc. and resulted as follows:

a. With the U. S. P. solution of stannous chloride: One cc.

gave no reaction during forty-five minutes, then gradual coloration began. If heat be applied the reaction begins in eighteen minutes and at the end of one hour is slightly more intense than when treated without heat. 1.5 cc. of reagent: reaction slightly more rapid and intense than with one cc. 2.0 cc. of reagent: still more rapid and intense, both with and without heating. 2.5 cc. of $SnCl_2$: reaction begins in fifteen minutes at air temperature in less than five minutes when heated. 3.0 cc. of $SnCl_2$: reaction slightly less intense than with 2.5 cc., both hot and cold. 3.5 cc. of reagent: a still further slight decrease in intensity. No difference could be observed in the reaction of As_2O_3 and As_2O_5; the sodium metarsenite appeared to be very slightly more colored than As_2O_3.

b. With one cc. of the U. S. P. solution and a small piece of metallic tin, at a temperature of about 80° C., one cc. of the solutions containing 0.05 mgm. of As, began showing a brownish color at thirteen minutes. At thirty-five minutes the reaction was quite sharp and continued to grow slowly in intensity to the end of the hour. No difference was perceptible between As_2O_3 and As_2O_5.

Three cc. of the solution of the "Arzneibuch" mixed with one cc. of the solutions containing 0.05 mgm. of As, began showing a feeble reaction at thirty-five minutes, and at the end of the hour showed a plain reaction as compared with the unchanged reagent, but did not equal in intensity, the reaction produced by the addition of metallic tin.

On repeating the experiments with solutions containing 0.03 mgm. of As in one cc., a feeble reaction resulted from the use of stannous chloride and metallic tin at the end of an hour, but even after standing over night the other methods gave such a faint reaction that it required close inspection in the colorimeter to perceive the change. A solution containing 0.02 mgm. of arsenic failed to show any reaction. So I think that for practical purposes the utmost limit of reaction is reached at 0.03 mgm. of As in one cc. and that the method employing metallic tin and heat is to be preferred where the presence of antimony or bismuth does not forbid its use. Even the addition of pure, concentrated sulphuric acid, which was recommended when the

test was first introduced, has not yielded to me any substantial advantage in detecting the presence of arsenic in greater dilutions.

II. The Best Proportion of Reagent to Specimen.

In the foregoing experiments and a number of others conducted for that purpose it was observed that both with the U. S. P. solution (without the use of metallic tin) and with that of the German pharmacopoeia, the greatest intensity of color obtained after an hour's reaction occurred when one cc. of the arsenical solution was mixed with 2.5 cc. of the reagent. Between three cc. and two cc. of the German solution hardly any difference could be found. But with the pale U. S. P. solution a very slight difference appeared in favor of two cc. as against three cc. Heat did not appear to affect the proportion needed.

When metallic tin was added it seemed to be best to use equal volumes of specimen and reagent, although the variable amount of dark coating of reduced arsenic adhering to the tin prevented an accurate comparison.

III. Influence of the Use of Metallic Tin Together With Stannous Chloride.

When metallic tin is heated with pure concentrated hydrochloric acid, a copious evolution of hydrogen results. When heated with the saturated solution of stannous chloride in hydrochloric acid, the evolution of hydrogen is but scant. When arsenic is mixed with the solution, the evolution of gas is perceptible but very feeble. Very little arsine appears to be evolved, for a paper cap with a drop of acidulated silver nitrate does not show any evidence of the reduction by AsH_3 for over fifteen minutes, and even at the end of an hour but a very faint arsenic reaction is seen.

To ascertain whether any of the arsine formed would react with the stannous chloride and thus hasten the reduction of As, I arranged a small apparatus in which a copious current of arsine, mixed with hydrogen, was generated and after passing through a bottle filled with dry cotton, was permitted to bubble through stannous chloride solution of the U. S. P. After more than an hour's time not a trace of coloration could be detected. So that after arsine has once been formed it is not again decomposed by

stannous chloride. Hence the prompt action of metallic tin must depend upon the *nascent* hydrogen, which aids the stannous chloride in reducing the trioxide and pentoxide.

But, however satisfactory the action of metallic tin in accelerating and intensifying the reduction of arsenic, it *cannot* be employed to detect arsenic in preparations of *bismuth or antimony*. For *the metallic tin reduces both of these metals*, and precipitates them from their solution as black floccules, which aggregate into small granular lumps. There could be a distinction made between the firm floccules of Sb or Bi and the finely divided brown particles of arsenic, but it would hardly be safe to trust to this appearance for a sufficient evidence of the presence of arsenic, and the preparations of Bi and Sb *must be tested without the aid of metallic tin*.

A number of specimens of pure bismuth and antimony salts were tested with the U. S. P. and the German solution of stannous chloride in various proportions. But neither at ordinary temperature nor when heated did the least coloring occur.

IV. Influence of the Presence of Other Substances in the Specimen Tested.

The preceding experiments were made with a solution of either arsenic trioxide or sodium metarsenite or arsenate in water, other substances being absent. But in testing various chemicals for traces of arsenic there are different conditions, as the arsenic forms only a very small portion of the mixture. In the U. S. P. the Bettendorf test is directed for eleven preparations. For hydrobromic, hydrochloric, phosphoric, and sulphuric acids, one cc. of the acid is to be tested by mixing with one cc. of the reagent, adding a small piece of tin-foil and heating. In case of magnesium sulphate, one gram of the dry substance is to be shaken with three cc. of the reagent; metallic tin is then to be added and an hour allowed for the appearance of the reaction; sodium phosphate, and pyrophosphate are treated in like manner, but heat applied and fifteen minutes time given.

In the case of antimony and potassium tartrate, antimony oxide, bismuth subcarbonate, and bismuth subnitrate, it was intended to test with stannous chloride alone for an hour, but by an unfortunate misunderstanding of the transcriber, tin-foil was

directed to be added, which will reduce Sb and Bi as well as As.

To find whether any of the chemicals directed to be tested by the stannous chloride method, could influence the detection of arsenic, specimens were prepared containing the pure chemicals shown to be free from arsenic by other tests, and with these small portions of arsenic were mixed and the tests compared with those in which arsenic was present in equal amount without admixture with the chemicals.

In no case could any difference in the intensity of the test be made out, nor were the differences in the time of the occurrence of the coloration sufficiently great or regular to justify the assumption that the reaction was impeded or accelerated by the presence of other salts.

ST. LOUIS, May 27, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY. No. 8.]

THE INFLUENCE OF ALUM, ALUMINUM HYDROXIDE AND ALUMINUM PHOSPHATE, ON THE DIGESTIBILITY OF BREAD.

BY W. D. BIGELOW AND C. C. HAMILTON.

Received June 28, 1894.

THE property which alum possesses of arresting the fermentation of flour, and making it possible to prepare presentable bread from very inferior flour has long been known, and the adulteration of flour by means of alum has been extensively practiced by millers and bakers. Comparatively little attention has been given to this subject in this country, but in Europe, especially in England, the question has been constantly before the minds of the public analysts for at least a quarter of a century. Indeed, as early as 1821 a law was passed prohibiting the addition of alum or any aluminum compound to flour or bread. This law remained in force till 1861 when it was repealed by the passage of a law which made it necessary for the prosecution to prove the injurious quality of the substance added.

It is universally admitted that the presence of alum as such not only impedes digestion but also exercises an injurious effect on the digestive organs. There is one phase of the alum question, however, to which a great deal of attention has been

given, both in this country and abroad; namely, the use of alum as the acid compound of baking powders. Unlike the practice of adding alum to flour or dough, this question has been attended with a long continued and fiercely contested controversy.

Many experienced analysts who have condemned alumed bread in unmeasured terms, have testified that in their opinion, bread baked with alum baking powders exercises no injurious influence on digestion or the digestive organs.

In the famous Norfolk[1] baking powder case, it was contended by the Government that alum united with the soluble phosphates of the flour with the formation of an insoluble compound, and that the flour was thus deprived of one of its most valuable constituents.

The defense, on the other hand, claimed that the aluminum was entirely precipitated as hydroxide. It is a curious fact that shortly after the Norfolk case the manufacturers of alum baking powders began the addition of acid calcium phosphate, and the position taken by prosecution and defense in the Norfolk case were reversed in a recent case[2] before the English courts. In the evidence submitted by the prosecution independent experiments were cited by Dunstan, Hehner, and Claude Thompson, to prove that aluminum hydroxide dried at 100° was soluble in two-tenths per cent. hydrochloric acid. Dunstan found aluminum hydroxide dried at 100° to be soluble in the gastric juice of a dog diluted to two-tenths per cent. of its normal strength, and that this fluid diluted to the same extent dissolved aluminum hydroxide from bread baked with the powder manufactured by the defendant.

Dunstan also found that aluminum hydroxide in bread interfered with the action of diastase (hence, with ptyalin, the digestive ferment of the saliva), and with peptic and pancreatic digestion. Also, that a three-tenths per cent. solution of sodium carbonate (the strength of the alkali in the intestinal juice) would dissolve aluminum hydroxide which had been dried at 100°. He also testified that he had found an aluminum salt in the urine of a man who had eaten one to two grams of aluminum hydroxide which had been dried at 100°.

Morgan testified that he had dissolved aluminum hydroxide

[1] *Analyst*, *1879*, **4**, 231, and *1880*, **5**, 21.
[2] *Analyst*, *1893*, **18**, 152; *Chem. News*, *1893*, **67**, 213.

which had been dried at 100° in his own vomit and in that of his son.

On the other hand, the defence took the ground that aluminum hydroxide was insoluble in the juices of the digestive organs. Sutton repeated Morgan's experiment, using as a dialyzer, however, a fresh sheep's bladder instead of a vegetable parchment as used by Morgan. Unlike Morgan he found no soluble aluminum compound in the dialysate. Luff cites an experiment intended to prove that dried aluminum hydroxide was insoluble in hydrochloric acid of the strength found in the gastric juice.

He took this strength of acid to be 0.02 per cent. instead of 0.2 per cent., the strength taken by the prosecution. His aluminum hydroxide also was heated to 150° instead of 100°, which is generally admitted to be the highest temperature attained by the interior of a loaf while baking, and he was not sure but the hydroxide might be changed to oxyhydroxide by heating to this temperature.

The work that has been done upon this subject seems to have been devoted to the influence of the gastric digestion alone, though J. West-Knights[1] and Dunstan,[2] working with diastase, reached the conclusion that the presence of alum, or of insoluble aluminum salts, interferes with the amylolytic action of ptyalin. Dunstan,[2] it is true, states that aluminum hydroxide interferes with pancreatic digestion, but appears to describe no experiment in proof of the statement.

J. West-Knights[1] found that gluten after treatment with alum, or its insoluble compounds, is about one-half less soluble in gastric juice than pure gluten, and pure bread is almost one-third more soluble than alumed bread in the same medium.

Pitkin[3] and Mallet[4] reached the conclusion that the aluminum compounds resulting from the use of alum baking powder were soluble to some extent in the gastric juice, while Patrick[5] found that when the dough was well mixed and bread well baked no aluminum hydroxide, resulting from the use of alum baking powder, was dissolved in the stomach of the cat. Hehner,[6] working

[1] *Analyst*, *1880*, **5**, 67.
[2] *Ibid*, *1893*, **18**, 152.
[3] *J. Am. Chem. Soc.*, *1887*, **9**, 27.
[4] *Chem. News*, *1884*, **58**, 276.
[5] *Analyst*, *1879*, **4**, 207; from *Sci. Am. Sup.*
[6] *Analyst*, *1892*, **17**, 201, and *1893*, **18**, 213.

with an artificial pepsin solution, found the detrimental influence of alum baking powder to be equal to that of alum in the digestion of egg and bread.

The suggestion has often been made that the water-soluble salts resulting from the use of an alum baking powder, such as ammonium sulphate and potassium sulphate, would be more likely to retard digestion than the insoluble aluminum compounds. It was to study this question with reference to gastric digestion, but more especially with reference to double digestion with gastric and pancreatic ferments, that we undertook the work which forms the basis of this paper.

For the preparation of samples, flour was obtained which was known to be free from alum and seven two-pound loaves were baked under our direct supervision. The bread was raised in every case by compressed yeast.

As soon as the bread was baked it was cut in thin slices, dried at a temperature of 98°, ground, and bottled.

I. Digestion of Bread Free from Alum and Aluminum Compounds.

Loaf No. 1 was found to contain 12.06 per cent. of albuminoids. Portions of two grams each were subjected to several methods of digestion. The results given are the means of closely agreeing duplicate or triplicate determinations.

1. *Digestion in Pepsin Solution.*—The pepsin solution here employed is that suggested by Wilson in his modification of Stutzer's method.[1] One gram of Merck's granulated pepsin was dissolved in one liter of 0.33 per cent. hydrochloric acid. Two grams of the dried bread, which had been previously extracted with ether, were placed in a flask with 100 cc. of the acid pepsin solution, placed in a water-bath and kept at 40°, with frequent shaking, for twelve hours. The contents of the flasks were then filtered and the residue washed, dried, and kjeldahled. It was found that 93.26 per cent. of the total albuminoids in the bread were digested,

2. *Stutzer's Method.*—Two-gram portions of the bread were then digested according to Stutzer's method, except that an

[1] *J. Soc. Chem. Ind.*, **10**, 118. See also Patterson in Report Maryland Experiment Station, *1891*.

artificial pepsin solution, as given above, was employed instead of a solution freshly prepared from the inner membrane of a hog's stomach. The residue from the pepsin digestion, after being thoroughly washed, was digested for six hours in 100 cc. of Stutzer's[1] pancreas solution. The extracted residue was then allowed to dry and the nitrogen determined by the Kjeldahl method. By this method 93.57 per cent. of total albuminoids were digested, only a slight increase over the amount digested by the pepsin solution alone.

3. *Stutzer's Method, Modified by Wilson.*[2]—The pepsin solution here employed was the same as in the preceding experiments. The pancreas solution was made by dissolving one and one-half grams of Merck's "absolute pure" pancreatin, and three grams of sodium carbonate in one liter of water. The well-washed residue from the pepsin digestion was digested for twelve hours in 100 cc. of this solution, with frequent stirring, a temperature of 40° being maintained in the water-bath in which the flasks were immersed. The residue was then filtered, washed, and the nitrogen determined by the Kjeldahl method.

By this method 93.21 per cent. of the total albuminoids were digested.

4. *Niebling's Method.*[3]—Two grams of the sample were washed with ether and introduced into a flask with 100 cc. of two-tenths per cent. hydrochloric acid. The contents of the flask were then heated to boiling and kept at that temperature for fifteen minutes, after which they were allowed to cool and were neutralized, or rendered very slightly alkaline with a solution of sodium carbonate. One hundred cc. of Stutzer's pancreas solution were then added (without previous filtration), and the flasks immersed in the water-bath, which was kept at the temperature of 37°–40° for six hours. The residues were then washed, dried, and kjeldahled.

[1] To prepare this solution take one kilogram of steer's pancreas which has been freed from fat as far as possible, pass through a sausage grinder, rub up in a mortar with sand and allow to stand exposed to the air twenty-four to thirty-six hours. Then add three liters of lime water, one liter of glycerol, sp. gr. 1.23, a little chloroform, and let stand from four to six days. Press through a bag and filter through filter paper. Before using, take 250 cc., add 750 cc. water containing five grams anhydrous sodium carbonate, heat to 37° to 40° for two hours and filter. *Landw. Versuchs-Stat.*, *1889*, **36**, 321–328. See also U. S. Department of Agriculture, Chem. Div., *Bull.*, **13**, part 8, 1028.

[2] *J. Soc. Chem. Ind.*, **10**, 118; through Report Maryland Experiment Station, *1891*, 338.

[3] *Landw. Jahrb.*, *1890*, **19**, 149–187.

The result showed that 93.28 per cent. of the total albuminoids were digested by this method.

5. *Niebling's Method, Modified.*—This method is the same as the one preceding except that the pancreatin solution given under Wilson's modification of Stutzer's method was used instead of Stutzer's pancreas solution. The sample was digested in the pancreatin solution for twelve hours. By this method, 93.21 per cent. of the albuminoids were digested.

It will thus be seen that closely agreeing results were obtained by the different methods of digestion with bread which was as free as possible from substances which might interfere with its digestion. It was next undertaken to ascertain the effect of alum on the same methods of digestion.

II. Digestion of Alumed Bread.

For this purpose two loaves of "alumed" bread were baked. The alum, in a fine powdered state, was thoroughly mixed with the flour before the dough was made. No. 1 contained eight-tenths gram, and No. 2, 428 grams crystallized alum in the two-pound loaf. As soon as baked the bread was dried, ground, and bottled as before. Loaf No. 1 contained 11.88 per cent., and No. 2, 12.06 per cent. albuminoids in the dried sample.

1. *Digestion in Pepsin Solution.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	89.11
2	4.28	80.98

From these figures it is evident that the digestion of albuminoids in a pepsin solution is greatly lessened by the presence of alum. This it is true is universally admitted, and the results of this method are merely given as confirmatory of the work of others.

2. *Stutzer's Method.*—By Stutzer's method, using, however, an artificial pepsin solution instead of the one used by Stutzer, the following results were obtained. Since all the alum would be removed by washing after the pepsin digestion in this method and the next, the amount of alum originally present was dissolved in a little water and added to the sample previous to the pancreatic digestion.

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.56
2	4.28	92.40

It will be seen that these results would lead us to a conclusion entirely different, and almost contradictory, to the one which we would obtain from the results of the pepsin solution alone. Before making further comment, however, let us examine the results obtained by the other methods of digestion.

3. *Stutzer's Method, Modified by Wilson.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.21
2	4.28	92.44

4. *Niebling's Method.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.54

5. *Niebling's Method, Modified.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.74
2	4.28	92.02

It is evident from these results that the custom of judging the influence of alum on the digestion by its effect on the digestion in the pepsin solution alone has led to grave errors. It is evident that the presence of alum interferes materially with the gastric digestion, but the aluminum seems to be precipitated by the alkali of the pancreatic fluid, so that a portion of the digestion which should be effected by the former ferment is effected by the latter. Of course, this paper does not take into consideration the toxic properties of alum, but we are led to believe that its influence on the digestion has been greatly overestimated.

III. Digestion of Bread Containing Aluminum Hydroxide.

It was next desired to ascertain the digestibility of bread which contained aluminum hydroxide but was free from the soluble salts which result from the use of baking powders. For this purpose two two-pound loaves of bread were baked, ground, and dried as before. Loaf No. 1 contained 0.54 gram of aluminum hydroxide, corresponding to about 3.24 grams of crystallized

alum. This amount might readily be obtained by the use of an alum baking powder. Loaf No. 2 contained two and one-half grams of aluminum hydroxide, a larger amount than should ever be found in bread.

This aluminum hydroxide was prepared by precipitation from an alum solution by means of ammonium hydroxide and washing with hot water till all soluble salts were removed. It was then heated to 100° till perfectly dry, and finely powdered in a mortar. The dried and powdered aluminum hydroxide was thoroughly mixed with the flour before the dough was made.

1. *Digestion in Pepsin Solution.*—As before stated, the evidence concerning the solubility of aluminum hydroxide which has been heated to 100° in the gastric juice is of the most contradictory description. Portions of two grams each of these samples were treated with 100 cc. of the acid pepsin solution with the following results:

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	87.03
2	2.50	86.78

According to these results the presence of aluminum hydroxide interferes materially with the digestion of albuminoids in a pepsin solution. We notice, however, that this retarding influence is not by any means proportional to the amount of hydroxide present. Indeed, although widely differing quantities of hydroxide were taken, their effect seems to be approximately the same. It seems probable, therefore, that even a much smaller amount of aluminum hydroxide might have given approximately the same results as the amounts employed. Concerning this point Hehner[1] found that when only a small amount of aluminum hydroxide was present its detrimental influence on the pepsin digestion was equal to that of an equivalent amount of alum, but when a larger amount was taken its effect was relatively less.

2. *Stutzer's Method.*—As before, a solution of Merck's granulated pepsin was used in this method in place of Stutzer's pepsin solution. The following results were obtained:

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	92.18
2	2.50	90.43

[1] *Analyst, 1893*, **18**, 213.

3. *Stutzer's Method, Modified by Wilson.*—

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	92.00
2	2.50	90.21

4. *Niebling's Method.*—

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	91.77
2	2.50	89.13

5. *Niebling's Method, Modified.*—

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	91.90
2	2.50	88.96

Methods 4 and 5 give results which are noticeably lower than were obtained by the other methods. Their lack of agreement with each other also is such as to cause a serious error if these methods were adopted for this work.

These results make it evident that with aluminum hydroxide, as with alum, the results by the pepsin digestion alone cannot be taken as a guide to the influence of the aluminum hydroxide resulting from the use of an alum baking powder on the digestion. Here, as with alum, the albuminoids whose digestion is prevented in the pepsin solution by dissolved aluminum compounds, seem to be almost all digested by the alkaline pancreas solution. It is true that the digestion is not quite as complete in the presence of alum or aluminum hydroxide as in their absence. It is possible that this is due to the presence of sodium aluminate in the pancreas solution.[1] Although it appears that the influence exerted on the digestion of albuminoids by aluminum hydroxide is very slight, the possible toxic effects of even the slight amount of aluminum chloride produced in the gastric juice should not be overlooked.

IV. Digestion of Bread Containing Aluminum Phosphate.

It seems to have been quite generally assumed that aluminum phosphate was much less soluble in the gastric juice than aluminum hydroxide, and that it would exert a correspondingly less influence on digestion. Indeed, some have gone so far as to

[1] See Dunstan, *Analyst*, *1893*, **18**, 152.

state that the only influence which could be exerted by the compounds resulting from an aluminum phosphate baking powder must be due to the soluble salts. In order to determine the effect of aluminum phosphate in the absence of the soluble salts, the preceding set of digestions was repeated with bread containing aluminum phosphate. Two two-pound loaves of bread were baked with the addition of aluminum phosphate and prepared for analysis as before. Loaf No. 1 contained 0.64 gram of aluminum phosphate, which is equivalent to 2.56 grams of crystallized alum. This amount has frequently been found in bread prepared by alum baking powder. Loaf No. 2 contained 3.20 grams of aluminum phosphate, an amount largely in excess of that usually found in bread.

For the preparation of this compound, alum was dissolved in water, an excess of hydrogen disodium phosphate added, and the resulting precipitate washed with water until the filtrate ceased to be acid. It was then dried at 100° and reduced to a fine powder in a mortar. The dried and powdered aluminum phosphate was thoroughly mixed with the flour before the dough was made.

1. *Digestion of Pepsin Solution.*—Portions of the samples were digested in the acid pepsin solution, as before, after washing with ether to remove the fat. The following results were obtained:

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	80.87
2	3.20	71.21

Comparing the result obtained in sample 1 with that obtained by the peptic digestion of alumed bread, we find that even when a relatively large amount of aluminum phosphate is present, its effect on the pepsin digestion is equal to that of an equivalent amount of alum. It is also apparent that its effect is much greater than that of an equivalent amount of hydroxide.

2. *Stutzer's Method.*—As in the previous digestions, this method was modified by substituting a solution of Merck's granulated pepsin for Stutzer's pepsin solution. The following results were obtained:

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	83.11
2	3.20	78.26

3. *Stutzer's Method, Modified by Wilson.*—

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	82.56
2	3.20	81.32

4. *Niebling's Method.*—

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	86.35
2	3.20	82.18

These results differ materially from those obtained by the other methods of digestion.

5. *Niebling's Method, Modified.*—

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	86.46
2	3.20	81.74

These results agree fairly closely with those obtained by method 4, but are materially lower than those obtained by methods 2 and 3.

From these results it appears that the influence of aluminum hydroxide on the digestibility of bread is about the same as that of an equivalent amount of alum, when present in about the quantity which is usually found as a result of the use of alum baking powder which contains no phosphate.

The action of aluminum phosphate is quite different, however, for notwithstanding the supposed insolubility of this compound, ten to twelve per cent. of the albuminoids which are digestible in the presence of alum or aluminum hydroxide appear to be insoluble in the presence of an equivalent amount of the phosphate.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY.—No. 9.]

SOME CHARACTERISTICS OF CALIFORNIA WINES.

BY W. H. KRUG.

AMONG the exhibits of American products at the World's Columbian Exposition, at Chicago, in the year 1893, one of the most interesting and varied was that of the California wine producers at the California State Building. The wines shown there, represented all the important districts in the state and the various types grown. At the suggestion of Dr. H. W. Wiley, Chief Chemist of the U. S. Department of Agriculture, the Cali-

fornia viticultural commission sent a set of these wines to the laboratory of the department, where they were analyzed under my supervision. All important varieties were represented and the analyses were made as complete as possible. The wines were classified as follows:

Dry White Wines—	36 of the Rhenish type.
	38 of the Sauterne type.
	6 of the white Burgundy type.
	7 miscellaneous.
Dry Red Wines—	37 of the Claret type.
	22 of the Medoc type.
	20 of the Burgundy type.
Sweet or Fortified Wines—	6 of the Sherry type.
	13 of the Port type.
	9 miscellaneous.
	—In toto, 194.

General Remarks.

California wine producers grow European types almost exclusively, and it will be seen from the table of analyses that they aim to follow these types in their description as closely as possible. This is carried even to the extent of adopting the various styles of bottles used in the European trade.

A few of the white wines were considerably deeper in color than the European wines of the same type. By far the greater number, however, were perfectly clear and brilliant, showing that great care had been exercised in maturing and preparing for bottling. This was especially true of the red wines. The following determinations were made:

Specific gravity, alcohol by weight, alcohol by volume, extract, total acidity as tartaric acid, polarization of 26.048 grams in a 200 mm. tube, polarization of the wine in a 220 mm. tube, Wild polariscope, reducing sugar as dextrose, glycerol, tannin and coloring matter, albuminoids, ash, sulphuric acid in ash, potassium sulphate in 100 cc. of wine stated in grams, chlorine in ash, sodium chloride in 100 cc. of wine stated in grams, insoluble residue in ash, sulphurous acid and salicylic acid.

In the sweet wines, the polarization was determined after inversion and after fermentation, the result being stated both in terms of 26.048 grams and of the original sample. The work on the

color intensity, and the presence of foreign coloring matters, has been delayed unavoidably and will not be ready in time for incorporation in this paper. It is intended to make this branch of the investigation especially complete.

Methods of Analysis.

Specific Gravity.—The specific gravity was taken on an analytical balance by means of a Westphal bob whose displacement had been previously determined.

Alcohol.—One hundred cc. of the wine were placed in a flask with fifty cc. of water and a little precipitated calcium carbonate, the flask attached to an upright condenser and the contents of the flask subjected to distillation. To prevent the volatilization of the alcohol, the condenser tube should be made to extend almost to the bottom of the receiver. A 100 cc. flask was used for a receiver, and when 100 cc. of the distillate had passed over, the operation was interrupted and the flask removed, shaken, and the specific gravity of the distillate determined in the same manner as given under specific gravity. The percentage of alcohol by volume was determined from the specific gravity by table II, on page 213, in Bulletin 38, Division of Chemistry, U. S. Department of Agriculture, and the percentage of alcohol by weight was determined by multiplying the percentage of alcohol by volume, by the specific gravity of absolute alcohol and dividing that product by the specific gravity of the wine.

Extract.—The direct method was used. In the case of dry wines, fifty cc. were weighed and evaporated on the water-bath to a sirupy consistence in a platinum dish about eighty-five mm. in diameter. The residue was dried two and one-half hours in a drying oven at 100°. Of the sweet wines only ten cc. were weighed and diluted with distilled water before being evaporated.

Total Acidity (expressed as tartaric acid).—Ten cc. of the wine were carefully measured into a beaker, diluted with distilled water, and a few drops of neutral litmus solution added. Decinormal sodium hydroxide solution was used in the titration, and the neutral point was determined by placing a drop of the liquid on delicate litmus paper. This was found to work equally well on white and red wines. A standard solution of calcium hydrox-

ide has been recommended for red wines, the end reaction being the appearance of a flocculent precipitate. I found it much more difficult, however, to observe this than to note the neutral point with sensitive litmus paper. Before this point is reached the natural coloring matter of the wine will change, indicating the approach of neutrality so that the operator can work without difficulty to within a tenth of a cubic centimeter.

Glycerol.—A. In dry wines. One hundred cc. of wine were evaporated down to about ten cc. on the water-bath with about five grams of fine sand. Milk of lime was then added until the reaction was strongly alkaline, and the evaporation carried almost to dryness. The residue was gently heated on the water-bath with about fifty cc. of ninety-six per cent. alcohol, and mixed with a glass pestle until a homogeneous paste was obtained. It was allowed to settle and the supernatant liquid filtered through a folded filter. The residue was repeatedly extracted in this manner until about 150 cc. of filtrate were obtained. To this a few pieces of glass or sand were added to prevent bumping, and the alcohol carefully distilled off over a small flame until about fifteen cc. remained. The evaporation was then continued on the steam-bath until the residue became sirupy. After cooling, it was dissolved in ten cc. of absolute alcohol and fifteen cc. anhydrous ether added, the flask well-stoppered and shaken. When the precipitate had collected on the sides of the flask, the clear liquid was decanted into a tared glass-stoppered weighing bottle capable of holding about fifty cc., the precipitate washed once or twice with a few cc. of a mixture of two parts of alcohol and three of ether, the washing being transferred to the weighing bottle. The ether-alcohol removed on the water-bath, the residue dried one hour in a water-oven and weighed. When the precipitate, caused by the addition of the ether, remains flocculent, it is separated by filtering through a small filter, which is then washed repeatedly with a few cc. of the ether-alcohol mixture.

B. In sweet wines. One hundred cc. of the wine are evaporated to a thick sirup on the water-bath with about ten grams of sand. The residue is repeatedly extracted with absolute alcohol until from 100 to 150 cc. have been used (the amount being

varied with the amount of sugar present). The extracts are united in a large flask and one and one-half parts ether added for every part of alcohol used. The flask is stoppered and allowed to stand until the liquid is clear. Almost all the sugar is present in the sirupy precipitate while the glycerol remains in solution. The clear liquid is decanted into a flask, the residue washed repeatedly with small quantities of the ether-alcohol mixture and the united liquids distilled. The evaporation is completed on the water-bath, the residue washed into a porcelain dish by means of a little water, and treated as in A.

Polarization.—The wines were all polarized in a Schmidt and Haensch instrument with a 200 mm. tube. In the case of the dry wines, fifty cc. were evaporated sufficiently to permit the addition of three cc. of lead subacetate solution and three cc. of a saturated sodium carbonate solution to the white, and respectively six cc. of each solution to the red wines. The precipitate was filtered off and the filtrate polarized. In the case of the sweet wines twenty-five cc. were taken and made up to fifty cc.

The sweet wines were both inverted and fermented. For inversion twenty-five cc. were placed in a fifty to fifty-five cc. flask, two and one-half cc. strong hydrochloric acid added. The flask was heated in a water-bath to 68° C., consuming about ten minutes in heating. It was removed, cooled quickly to room temperature, filtered, and polarized. For fermentation, fifty cc. were placed in a wide-mouthed flask, a quarter of a cake of Fleischmann's compressed yeast and a sufficient amount of a potassium fluorid solution added, so that ten mgms. of this salt were present. The flask was allowed to stand four days at room temperature when it was found that fermentation was complete. The liquid was then washed into a 100 cc. flask, four cc. of lead subacetate solution, two cc. of mercuric nitrate solution (U. S. Department of Agriculture, Division of Chemistry, Bulletin 38, p. 198), and a varying amount of thick alumina cream added. It was then made up to 100 cc. with water, filtered, and polarized. The mercuric nitrate solution was added to destroy any bacteria which might impair the transparency of the filtrate when the latter, by any chance, stood for a length of time before being polarized.

If, after inversion, the wine polarizes more strongly to the left, unfermented cane sugar is present.

If, after fermentation, it polarizes to the right, the unfermentable constituents of commercial glucose are probably present.

Reducing Sugar.—This was determined by Allihn's gravimetric method and was calculated as dextrose.

Reagents.—1. 34.639 grams of crystalline copper sulphate dissolved in water and diluted to 500 cc.

2. One hundred and seventy-five grams of Rochelle salt.

One hundred and twenty-five grams of potassium hydroxide.

Dissolved in water and diluted to 500 cc.

In white wines. Fifty cc. were neutralized with sodium carbonate, the alcohol removed by heating on the steam-bath, made up to the original volume with water and filtered through a dry filter. When necessary, this solution was diluted with water to bring the reducing sugar down to one per cent. or less.

Thirty cc. of the copper solution, thirty cc. of the seignette solution, and sixty cc. of water, were placed in a beaker and heated to boiling. Twenty-five cc. of the sugar solution were then added and the whole boiled two minutes. The cuprous oxide was immediately filtered off and washed with hot water. It was then dissolved in dilute nitric acid, reduced to copper by the usual electrolytic method and weighed in that form.

The red wines were decolorized by filtering through bone-black, the first portion being rejected and the second portion treated precisely as the white wines.

Tannin and Coloring Matter.—The Löwenthal method was used.

Reagents.—Permanganate of potash solution: 1.333 grams of crystallized potassium permanganate in a liter of water.

Indigo solution: Six grams of sodium indigo sulphate and fifty cc. concentrated sulphuric acid per liter of water.

Decinormal oxalic acid solution.

Washed bone-black suspended in water so as to make a thin paste.

A. One hundred cc. of wine were dealcoholized by boiling and the lost weight restored with water. Ten cc. of the dealcoholized wine are transferred to a large porcelain casserole, twenty

cc. of the indigo solution and about 750 cc. of distilled water added, and the titration carried out with the permanganate solution, adding a cubic centimeter at a time until the liquid becomes green, when it is added drop by drop until the color turns to golden-yellow. Result A.

B. Ten cc. of the dealcoholized wine are diluted with water, a few cc. of the bone-black added, the liquid well stirred with a glass rod and allowed to stand some time. The bone-black is then filtered off and washed repeatedly with water. The filtrate is diluted to about 750 cc. and titrated as in A after adding the indigo solution. Result B.

Result A—Result B=cubic centimeters required by the tannin and coloring matter. This is stated in terms of oxalic acid.

Ash.—The residue from the extract determinations was carefully incinerated and weighed. In the sweet wines, the ash was determined by charring the extract and exhausting with hot water. The insoluble residue, consisting mostly of carbon, was collected on a filter, washed, dried, and burnt separately, the residue from the water extract was added to this and the whole heated to low redness until white.

Albuminoids.—The Kjeldahl method was used, the wine being previously evaporated to dryness in the digestion flasks. The amount used varied with the wines, it being necessary to use as little as ten cc. of some of the sweet wines on account of the tendency to foam when digested with sulphuric acid.

Sulphuric Acid and Chlorine in the Ash.—The ash was digested with hot water and a few drops of nitric acid and filtered into a fifty cc. flask. The residue was washed with hot water until the flask was full to the mark. It was cooled, made up and the sulphuric acid estimated in an aliquot portion in the usual manner. In another portion the chlorine was determined volumetrically with $\frac{N}{200}$ silver nitrate solution. They were respectively converted to grams potassium sulphate and sodium chloride in 100 cc. of wine.

Insoluble residue in Ash.—The filter and residue were ignited in a weighed platinum crucible and weighed.

Sulphurous Acid.—In the determination of sulphurous acid 100 cc. of the wine were diluted in a distilling flask with fifty

cc. of water, acidulated with five cc. of dilute sulphuric acid (H_2SO_4 one part, H_2O, three parts). The distillation was carried on in an atmosphere of carbon dioxide and the distillate received in a flask containing a measured quantity of decinormal iodine solution. The condenser tube should extend well below the surface of the iodine solution and in case a current of carbon dioxide be passed through the apparatus, the receiving flask should be closed with a mercury valve or attached to a U tube containing a portion of the iodine solution. In the progress of the work it was found more convenient to expel the atmosphere by the addition of a small quantity of sodium carbonate and in this case the guard-tube was found to be unnecessary. After about 100 cc. have distilled over, the excess of iodine is determined with decinormal sodium thiosulphate solution.

Salicylic Acid.—The following method was worked out by Mr. W. D. Bigelow who had charge of this branch of the investigation.

Seventy-five cc. of the wine are placed in a separatory funnel, acidified with five cc. of dilute sulphuric acid (H_2SO_4 one part, H_2O three parts) and extracted with a mixture of eight parts of sulphuric ether and one part of petroleum ether. The ether is washed once with water and then thoroughly shaken with about twenty-five cc. of water and six to eight drops of a five-tenths per cent. solution of ferric chloride. The aqueous layer contains most of the coloring matter in combination with the iron and is discarded. The ether is then washed with water, transferred to a porcelain dish, evaporated to dryness and the residue heated to the full temperature of the steam-bath for a few minutes. When the dish has become cool from four to five cc. of water are added, the insoluble matter filtered off after a few minutes and the filtrates tested for salicylic acid by the addition of three to four drops of a five-tenths per cent. solution of ferric chloride. By this method an excellent clarification may be obtained with white wines and with most red wines. Sometimes, however, with the latter, a second extraction is necessary.

General Remarks Concerning the Methods of Judgment.

There being no law in this country which governs and regu-

lates the chemical composition of wines it was deemed advisable to apply some foreign standard. It is true that our wines grown under different climatic and soil conditions cannot be judged with absolute fairness by a standard based on the composition of European natural wines. Such application can only be of value as a means of comparison and was applied only in such sense.

The standards used were those adopted in the German Empire. On account of the lengthiness of the report made by the Royal Commission empowered to frame the regulations, I will only mention the more salient points relating to the constituents of wine. They are as follows:

Wines which have been prepared solely from pure grape juice contain only rarely less than one and one-half grams extract per 100 cc. If, therefore, a wine is found to contain less it must be rejected unless it can be proved that other wines of the same type and year exhibit the same peculiarity.

After deduction of the "fixed acid" the extract-rest in natural wines equals at least one and one-tenth grams per 100 cc., after deduction of the total acid at least one gram.

A wine in which the ash equals more than ten per cent. of the extract, should contain a correspondingly larger amount of extract than is usually assumed to be a minimum. In natural wines the ash and extract are very often found to be in the proportion of one to ten. A considerable variation from this ratio, however, does not justify the assumption that the wine is adulterated.

In accordance with experience the free tartaric acid does not amount to more than one-sixth of the "fixed acids."

The ratio between glycerol and alcohol can vary in natural wines from 7 : 100 to 14 : 100. Wines having a different ratio have had either alcohol or glycerol added to them.

As during the various manipulations which the wine undergoes, small amounts of alcohol (not more than one per cent. volume) may get into the wine, this must be considered in judging wines. The above limits and ratios are not always applicable to sweet wines.

For the individual inorganic constituents no reliable limits

can be given. The supposition that better wines always contain more phosphoric acid is without foundation.

Wines containing less than 0.14 gram ash per 100 cc. must be rejected unless it is shown that other natural wines of the same type and year show the same peculiarity.

Wines containing more than 0.05 gram NaCl in 100 cc. must be rejected.

Wines containing more than 0.092 gram of SO_3 per 100 cc. (corresponding to two grams of K_2SO_4 per liter) must be designated as having been treated with gypsum, *i. e.*, plastered.

Various circumstances or influences can make a wine ropy, dark, brown, turbid, or bitter, or can change its color, taste, and odor. The coloring matter of red wines may thus be precipitated. None of the above phenomena justify the assumption that the wine is not genuine.

A second fermentation in a wine does not absolutely indicate the addition of sugar or sweet substances. Very often the original fermentation is hindered, or a sweet wine may have been added to the original completely fermented wine.

In only a few samples were deposits noticeable, most of the wines, both white and red, presenting a fine appearance and showing that they were well-matured before being bottled. Deposits were much more prevalent among the white than among the red wines. In the analytical tables, the wines are classified by types, and this classification is followed in the discussion as far as practicable.

To facilitate discussion of the results the most important points were arranged as follows:

1. Are substances present which are not characteristic of pure natural wines and deleterious to health?

2. Is the quantitative composition of the wines such as is shown by European natural wines?

3. In what manner have the manipulations varied from those used in the preparation of pure natural wines?

First.—Are substances present which are not characteristic of pure natural wines and deleterious to health?

Such substances may be unfermented cane sugar, the unfermentable constituents of glucose, potassium sulphate, sodium

chloride, sulphurous acid, and other preservatives. Some interesting data were obtained in this connection.

Among the twenty-eight sweet wines there was only one, Port, No. 12,814, that gave a zero polarization after fermentation. In every other instance, as will be seen from the tables, there was a dextro rotation showing possibly that commercial glucose had been used for purposes of fortification. It is well-known, however, that this substance is not used in California, and, therefore, this dextro rotation is not positive proof of the use of glucose. All but five gave an increased left-handed reading after inversion, indicating the presence of non-inverted sucrose. Although there can be no objection to the presence of sucrose or invert sugar, it has not been determined as yet whether the unfermentable constituents of glucose, the most important of which is amylin, exert any specific physiological action on the human body, and as long as this is the case any decision on their injuriousness must be withheld.

To produce sweet wines it is absolutely necessary to add some saccharine substance to obtain the desired strength in alcohol and requisite sweetness. It would be much more rational, however, for the producer to use cane sugar, which can be procured pure so easily, especially as it has hitherto been impossible to obtain pure dextrose at a price which would render its use profitable.

There were found only three wines which exceeded the German limit for potassium sulphate; namely, Gutedel, No. 12,678, with 2.321 grams per liter, Zinfandel, No. 12,713, with 2.392 grams per liter, and Burgundy, No. 12,714, with 2.315 grams per liter, the latter two being from the same winery. Plastering is therefore not used very much to excess by California wine producers. Plastering is the commercial term applied to the treatment of the grapes with burnt gypsum. All Spanish, Italian, and Greek wines are extensively plastered. In Greece, a layer of grapes is placed in a low cistern and well-covered with gypsum, which is followed with another layer of grapes in turn covered as before, this being continued until the cistern is full. After from twelve to twenty-four hours the grapes are mashed by treading and the must filled in casks. The use of gypsum

secures a quicker ripening and better color. The chemical changes taking place are, in brief, as follows:

The potassium bitartrate and calcium sulphate react forming calcium tartrate and potassium acid sulphate, of which the former, on account of its insolubility, separates almost entirely during fermentation. This insolubility is also the cause of the rapid clearing of the wine after fermentation. The improved color of a wine thus treated is stated by Kayser to be due to the presence of free phosphoric acid. Plastering has become very popular in France, as it enables the producers to supply a cheap red wine by avoiding the expense attached to a long period of ripening. Plastered wine contains the same amount of potash as the must, while in a natural wine the precipitation of potassium bitartrate decreases the potash more or less. Pure must contains rarely as much as two-tenths gram of SO_3 per liter, while in plastered wines this is greatly exceeded, often amounting to eight-tenths to two grams per liter. Plastered wines always show a higher ash than natural wines. Thus a wine of from eight to ten volume per cent. alcohol and 2.2–2.3 grams extract per 100 cc., which normally contains 0.2–0.25 gram of ash per 100 cc. will, after plastering, contain 0.28–0.35 gram. A plastered wine made from pure must will always contain at least one-tenth gram of potash per 100 cc., and usually considerably more.

From a physiological standpoint the only objection to plastered wines is the presence of potassium sulphate. Although it is evident that the consumption of a large quantity of such wines would be necessary to produce a physiological action on a normal individual, it must likewise be considered that much smaller quantities may be harmful to invalids and children. When we keep the fact in mind that the southern sweet wines are the ones preferred for medicinal use, and at the same time the ones most extensively plastered, we can appreciate the force of these remarks. None of the California sweet wines analyzed exceeded the limit, two grams per liter, although one, Port, No. 12,710, approached it with 1.861 grams per liter.

All the dry white and the sweet wines, with the exception of the Ports and Sherries, were examined quantitatively for sul-

phurous acid and only twelve were found that contained none. In every other case the amount present exceeded the limit placed by the German law. Even when we adopt the limit suggested by the Association of Bavarian Representatives of Applied Chemistry; namely, 0.01 gram per liter, we find that all the wines analyzed that were found to contain sulphurous acid exceed this by far. They are sulphured excessively. Sulphuring is, without doubt, one of the most important adjuncts to the manufacture of wine.

The use of sulphurous acid is very old. Arnolf de Villanova mentions it in his work on wine manufacture printed in 1830 and von Holburg in 1587 recommended the use of sulphur to fumigate the casks and directed to burn three sticks and then close the cask so as to retain the fumes. He found that this insured good and perfect wines that did not deteriorate on standing. In a book published in Nuremberg in 1708 entitled "Der Kuriose Kellermeister," the amount of sulphur required for a 600 liter cask is given as seventeen grams. In a book published in 1775 under the title "Treatise on the Improvement of Wine and the Prevention of Injurious Practices in Wine Making." This statement is made on page 75: "Fumigation is necessary and important, first to preserve the wines and cask and second to improve the wine."

Only twice have attempts been made to replace sulphur. Once when the use of alcohol was suggested and again when it was believed that an ideal preservative had been found in synthetic salicylic acid. Neither realized the expectations of its promoters and sulphuring to-day still holds the same position that it has for centuries. Sulphuring is used to fumigate the casks, to prevent oxidation in the wines, and to prevent diseases peculiar to the wines.

Technically the use of sulphur is, without doubt, wrong. Wine ages by a slow process of oxidation which is absolutely interrupted as long as any sulphurous acid is present. As a preservative, sulphurous acid in the amount used is not an unqualified success as is shown by the necessity of repeating sulphuring when a wine stands for some time before being consumed. Nessler found that from thirteen to eighty-one mgms.

per liter were required to prevent the browning and turbidity of red wines. Moritz found that the growth of mycoderma vini was not indefinitely hindered until 0.05 per cent. sulphurous acid was present. All these figures far exceed the limits of the European laws.

From a physiological standpoint the presence of sulphurous acid is objectionable not so much on account of any possible immediate action but more through the cumulative effect on the digestive tract. Such effects will rapidly become general throughout the whole nervous system. In connection with this the experiments of Braun and Bematzik are of interest. They are the only ones made on man and showed that doses of eighty mgms. upwards caused serious irritation of the alimentary canal. Husemann and Bischoff recorded several cases where the consumption of freshly sulphured wine caused physiological disturbances and severe headache in persons otherwise accustomed to wine.

A further objection is the formation of bisulphates and even of free sulphuric acid in frequently sulphured wine. These also have a physiological action which cannot well be overlooked.

Eighty-seven wines were examined for sulphurous acid. Thirty-three of those contained more than eighty mgms. sulphurous acid per liter. Of these twenty-nine contained over 100 mgms., nine of 200 mgms., and two over 300 mgms.

All wines were examined for salicylic acid and only four were found to contain this preservative; namely, Sauterne No. 12,631, heavy reaction; Claret No. 12,633, very heavy; Port No. 12,627, distinct; and Port No. 12,710, heavy. It is hardly necessary to explain the objections against this preservative and it is a pleasure to find it so little used by wine producers in California. Nos. 12,627, 12,631, and 12,633 are wines from the same firm.

Second.—Is the quantitative composition of the wines such as is shown by natural wines?

All the wines analyzed show when compared with European wines one striking difference, their much lower glycerol-alcohol ratio. According to the German law this should not be lower than seven nor higher than fourteen, sweet wines to be excepted. A glance at the analyses will show that in California wines it

rarely rises to eight or above and that the average is from five to six. Baumert in his work on seven California wines also found this to be the case and makes the assertion that it is due to a slight alcoholizing of the wines. In our work we have, however, found it to be a general characteristic and it hardly seems possible that wine producers should practice this mode of fortification so universally. I am rather inclined to believe that the proper solution of the problem will be found in a careful study of the processes of fermentation as they take place in the California wines. It is probable that the fermentation takes place too rapidly to permit of the formation of a proper quantity of glycerol.

A comparison between the composition of California wines and European wines of the same type is difficult as the propriety of applying the same form of judgment to two kinds of wine grown under different conditions of soil and climate is doubtful. Still it may be of interest to call attention to the points wherein they differ.

For purposes of comparison the analyses given in König, Chemie der menschlichen Nahrungs-und Genussmittel were used.

Wines of the Rhenish Type.—The California Riesling is distinguished according to these analyses by a higher alcohol and lower extract content, and a somewhat lower acidity. The percentage of glycerol present is in most cases much lower. The California Riesling varies from 8.45–11.67 per cent. alcohol by weight, 1.66–2.61 per cent. extract, 0.478–0.658 per cent. total acid as tartaric acid, and 0.501–0.932 per cent. glycerol, while German Riesling varies from 5.90–10.15 per cent. alcohol by weight, 1.7–3.21 per cent. extract, 0.395–1.250 per cent. total acid as tartaric acid, and 0.49–1.34 per cent. glycerol.

California Gutedel, on the other hand, is higher both in alcohol and extract, while the acidity is somewhat lower. It varies from 9.67–11.16 per cent. alcohol by weight, 1.67–2.34 per cent. extract, and 0.467–0.662 per cent. total acidity. German Gutedel shows from 7.12–8.23 per cent. alcohol by weight, 1.67–2.01 per cent. extract and 0.241–0.830 total acidity. The California wine shows in accordance with its higher percentage of extract a higher ash than the German wine.

No analyses of German Hock could be found, so it is impossible to draw comparisons on this wine, though its close agreement with the two wines just discussed makes it highly probable that it will exhibit the same characteristics. In general, these wines are all somewhat stronger in alcohol and higher in extract than the German wines of the same type.

Wines of the Sauterne Type.—A comparison of the minima and maxima and means of American Sauterne with those of French Sauterne show that although the average California Sauterne shows a higher alcohol content, wines are found on the French market that exceed the highest found in our work. California Sauterne shows a lower extract and acidity, while the percentage of glycerol is far below that found in French wines. The following figures will exibit this. California Sauterne: Alcohol by weight, 8.43–12.18 per cent., extract, 1.7–4.03 per cent., acidity, 0.422–0.641 per cent., and glycerol, 0.178–0.850 per cent. French Sauterne: Alcohol by weight, 9.05–12.49 per cent., extract, 2.47–3.54 per cent., acidity, 0.54–0.75 per cent., and glycerol, 0.866–1.03 per cent.

The same general characteristics are true of the other miscellaneous California white wines analyzed. On the whole, all these wines exhibit a higher alcohol, somewhat lower extract and acidity, and a much lower percentage of glycerol.

Wines of the Claret Type.—The various California representatives of the Claret type, the most important of which is the Zinfandel, all show a higher percentage of alcohol, extract and total acid, and a lower glycerol content than the French Clarets. California Zinfandel shows the following minima and maxima: Alcohol by weight, 9.15–10.5 per cent., extract, 2.28–3.37 per cent., total acidity, 0.635–0.871 per cent., glycerol, 0.446–0.634 per cent. California Claret gives the following figures: Alcohol by weight, 9.16–11.23 per cent., extract, 2.36–3.34 per cent., total acidity, 0.601–0.783 per cent., and glycerol, 0.484–0.620 per cent. French Clarets vary within the following limits: Alcohol by weight, 7.45–9.32 per cent., extract, 2.0–3.0 per cent., total acidity, 0.47–0.78 per cent., and glycerol, 0.55–0.99 per cent. In accordance with the higher extract a higher ash was found in California Clarets; *viz.*, 0.235–0.342 per cent., French Clarets giving 0.19–0.31 per cent.

Wines of the Medoc Type.—These wines are represented in California by the Cabernet, Malbec and Medoc. Only the last could be compared with French wines, no analyses of wines of the first two subtypes being found. Here it was again found that the California wines were characterized by a higher percentage in alcohol, extract and acidity, while the glycerol was much lower than in the French Medocs.

The following minima and maxima were obtained. California Medocs: Alcohol by weight, 11.75–12.4 per cent., extract, 2.33–2.92 per cent., acidity, 0.614–0.824 per cent., and glycerol, 0.371–0.556 per cent. French Medocs: Alcohol by weight, 9.50–10.70 per cent., extract, 1.96–2.60 per cent., total acidity, 0.380–0.680 per cent., and glycerol, 0.640–1.04 per cent. Corresponding to the higher extract a higher ash was found in the domestic wines; *viz.*, 0.304–0.386 per cent. French Medocs showing from 0.21–0.297 per cent.

Wines of the Burgundy Type.—Only one analysis of a Burgundy wine was in König. A comparison with this showed the California Burgundies to contain a higher percentage of alcohol, extract, acidity, and ash than French Burgundy, while the glycerol is lower. The following minima, maxima, and means were obtained:

CALIFORNIA BURGUNDY.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by volume	10.97	15.48	12.57
Extract	2.20	3.48	2.79
Acidity	0.594	0.783	0.674
Ash	0.190	0.362	0.283
Glycerol	0.464	0.640	0.551

CALIFORNIA MATARO.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by volume	9.58	13.40	12.38
Extract	2.24	3.39	2.79
Acidity	0.601	0.837	0.673
Ash	0.203	0.322	0.278
Glycerol	0.544	0.583	0.553

French Burgundy: Alcohol by volume, 11.23 per cent., extract, 2.63 per cent., acidity, 0.390 per cent., ash, 0.210 per cent., and glycerol, 0.680 per cent.

A general comparison of all California dry wines shows, therefore, that they are characterized by a high percentage of alcohol and low percentage of glycerol. In the white wines, the extract, acidity and ash are generally lower than in foreign wines while in the red wines these constituents are higher.

Sweet Wines.

Wines of the Sherry Type.—California Sherries on the whole are lower in alcohol than Spanish Sherries. They are higher in extract, which is due to the presence of unfermented grape sugar. The total acidity is higher while the ash and glycerol are lower. Following are the minima and maxima: California Sherry: Alcohol by weight, 14.38–17.57 per cent., extract, 3.33–9.38 per cent., acidity, 0.378–0.797 per cent., reducing sugar, 1.20–6.17 per cent., ash, 0.211–0.420 per cent., and glycerol, 0.325–0.722 per cent. Spanish Sherries: Alcohol by weight, 16.01–19.88 per cent., extract, 2.69–5.40 per cent., acidity, 0.250–0.640 per cent., reducing sugar, 0.52–3.77 per cent., ash, 0.200–0.660 per cent., glycerol, 0.220–0.910 per cent.

Wines of the Port Type.—These wines exhibit in general the same characteristics in comparison with Portuguese Ports as the Sherries; namely, a slightly lower percentage of alcohol, and a higher extract and acidity. The glycerol is in these wines slightly higher. The high extract is due to the presence of unfermented grape sugar. The following data were obtained: California Ports: Alcohol by weight, 11.97–17.40 per cent., extract, 8.52–16.51 per cent., acidity, 0.412–0.674 per cent., reducing sugar, 5.16–13.00 per cent., and glycerol, 0.161–0.688 per cent. Portuguese Ports: Alcohol by weight, 15.71–17.87 per cent., extract, 6.69–9.90 per cent., acidity, 0.290–0.470 per cent., reducing sugar, 4.42–8.12 per cent., and glycerol, 0.230–0.710 per cent.

Comparison of California Muscatel with Other Wines of that Name.

California Muscatel approaches the Syrian Muscatels in its alcohol content. No strict comparisons can be drawn between it and Sicilian Muscatels as the latter vary within too wide limits. It is stronger in alcohol and has in general a lower extract than the Greek Muscatels, due no doubt to the fact that

a large quantity of concentrated must is added to the finished wine in Greece so as to obtain a very sweet product. The glycerol content is higher and the ash and total acidity lower than in foreign Muscatels.

The following minima and maxima will show the differences existing:

CALIFORNIA MUSCATEL.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by weight	10.45	15.50	13.63
Extract	17.01	18.62	17.55
Acidity	0.317	0.405	0.369
Reducing sugar	43.18	16.30	14.66
Glycerol	0.866	1.014	0.941
Ash	0.148	0.192	0.113

SYRIAN MUSCATELS.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by weight	10.67	15.26	13.63
Extract	4.22	18.86	9.76
Acidity	0.430	0.830	0.646
Reducing sugar	0.25	4.50	3.13
Glycerol	0.320	2.00	0.857
Ash	0.210	0.960	0.495

GREEK MUSCATELS.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by weight	9.44	11.62	10.57
Extract	13.32	24.13	15.27
Acidity	0.410	0.751	0.566
Reducing sugar	13.50	18.86	15.01
Glycerol	0.564	0.950	0.718
Ash	0.290	0.388	0.321

SICILIAN MUSCATELS.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by volume	6.00	24.66	15.34
Extract	3.56	38.18	20.08
Acidity	0.270	1.140	0.630
Reducing sugar	12.50	29.01	17.16
Glycerol	....	....	....
Ash	0.170	0.860	0.410

Five other samples of sweet wines were analyzed; namely, three Angelicas, one Tokay, and one Catawba. Of these, the Tokay is the most interesting as it differs in every respect from

the Hungarian Tokays. The percentages of alcohol and glycerol present are much higher; the extract, reducing sugar, acidity, and ash, lower. It is a more completely fermented wine.

Third.—In what manner have the manipulations differed from those employed to produce a pure natural wine?

With the exception of the extensive use of sulphur very little can be said against the dry wines. They are almost all well fermented and matured grape juice. All the white wines but twelve have been excessively sulphured, three exceeded the limit for potassium sulphate, and four contained salicylic acid.

Two wines of the Sauterne type, Nos. 12,653 and 12,775, were excluded from the averages as evidently not representative wines, No. 12,653 gave 6.69 per cent. extract, and 3.52 per cent. reducing sugar, while No. 12,775 gave 5.48 per cent. extract. The glycerol was respectively 0.432 and 0.456 per cent. They were evidently incompletely fermented wines.

No. 12,792, a dry white wine, proved an interesting sample. It furnished the following figures: Alcohol by weight, 9.53 per cent., extract, 1.1 per cent., glycerol, 0.321 per cent., ash, 0.191 per cent., ash extract ratio, 17.36 per cent., extract-rest, 0.56 per cent. There is no doubt in my mind that this is merely an artistic mixture that never saw a vineyard but had its birth in the cellar of some wine mixer.

Another sample, No. 12,684, a miscellaneous red wine, gave only 0.105 per cent. total acid. The manufacturer here, no doubt, has used chaptalization to reduce the acidity and succeeded beyond his expectation.

Cane sugar is undoubtedly used by many to sweeten their wines, as is shown by the increased laevo rotation after inversion.

On the whole, it is evident that the California dry wines are fully equal to the European wines, and the red wines are in every respect superior to the young French Clarets. The sweet wines are to be unconditionally preferred to the European southern wines containing the same amount of alcohol and extract, and not being plastered. Their superiority is already being appreciated in Europe, and it is only a question of time when an extensive foreign market will be open to this, one of our most promising home products.

The Influence of Commercial Glucose on the Polarization After Fermentation.

To determine this point, a number of fermentations were made with mixtures of solutions of sucrose and glucose of varying strength, the same method being used as was employed in the analytical work. The results were not as uniform as desirable, probably on account of unequal rate of fermentation. They showed, however, that the amount of sucrose which is apt to be present in a wine is completely fermented in two days, so that any dextro rotation observed after that time must be due to the presence of glucose or its non-fermentable constituents.

Table of Results of Experiments Made to Determine the Effect Commercial Glucose has on the Polarization after Fermentation.

Original polarization of sucrose.	Original polarization of glucose.	Polarization after two days.	Polarization after four days.
+37 80	.....	0	0
+18.90	.....	0	0
+ 9.45	.....	0	0
.....	+16.33	+4.5	+5.0
.....	+16.33	+4.8	+3.8
.....	+ 9.80	+2.0	+1.8
.....	+ 9.80	+2.5	+1.8
.....	+ 3.27	+0.4	0
.....	+ 3.27	+1.0	0
+19.23	+16.33	+4.6	+2.8
+19.23	+16.33	+3.5	+3.3
+11.54	+16.33	+3.5	+2.3
+11.54	+16.33	+3.0	+2.3
+ 3.85	+16.33	+3.7	+2.4
+ 3.85	+16.33	+3.6	+3.9
+19.23	+ 9.80	+2.0	+1.7
+19.23	+ 9.80	+2.8	+2.1
+19.23	+ 3.27	+0.7	+0.9
+19.23	+ 3.27	+0.7	+0.5
+11.54	+ 9.80	+2.4	+1.0
+11.54	+ 9.80	+2.3	+1.0
+ 3.85	+ 9.80	+0.9	+0.3
+ 3.85	+ 9.80	+0.8	+0.3

[Contributions from the Chemical Laboratory of the U. S. Department of Agriculture, Sent by H. W. Wiley.—No. 10.]

CONTRACTION OF AQUEOUS SOLUTIONS OF ACETONE.

By K. T. P. Mc Elroy.

IN the following determinations, mixtures of known weights of acetone and water were made, the specific gravity determined by a piknometer and from this figure the volume calculated. The acetone used was bought from a New York firm and was of good purity, being free from methyl alcohol. It was fractionated and the fraction retained was boiled over calcium chlorid under a reflux condenser for three days. This portion was once more fractionated. The portion finally used boiled at 56.4° (air). Other samples were prepared for comparison by distilling acetates and by purifying the New York article by means of the sulphite compound. These various preparations possessed essentially the same boiling points and specific gravity.

In detail the method employed was to weigh a flask, add water, weigh, add acetone, reweigh, mix the united fluids by shaking and finally determine the specific gravity, first at 20° and then without refilling the piknometer, at 25°. The figures thus obtained are given in the annexed table:

Table I.

Weight acetone. Grams.	Weight water. Grams.	Acetone. Per cent.	Water. Per cent.	Total weight. Grams.	Specific gravity 20°.	Specific gravity 25°.
39.7256	2.0878	95.01	4.99	41.8134	0.80717	0.80174
37.4627	4.1328	90.09	9.91	41.5955	0.82172	0.81626
33.4936	4.6211	87.88	12.12	38.1147	0.82784	0.82278
32.3374	8.0688	80.04	19.96	40.4062	0.84972	0.84443
30.1632	10.0480	75.02	24.98	40.2112	0.86342	0.85796
28.1373	12.0375	70.04	29.96	40.1748	0.87495	0.87051
24.2140	16.1070	60.06	39.94	40.3210	0.89920	0.89469
20.1621	20.0854	50.10	49.90	40.2475	0.92078	0.91656
16.1438	24.1902	40.03	59.97	40.3360	0.94057	0.93695
12.5495	28.1583	30.83	69.17	40.7078	0.95606	0.95286
8.0333	32.8027	19.67	80.33	40.8360	0.97270	0.97024
4.0120	36.0740	10.01	89.99	40.0860	0.98507	0.98337

In table II these weights are recalculated into volumes at 20° and the per cent. of contraction for that temperature calculated. The figures representing the weights of the acetone were divided by the specific gravity of acetone at 20° (0.79197) and the volume

occupied at that temperature thus found. The same operation performed on the weight of the water, using the figure 0.99826, gave the volume of that liquid. These two volumes added together gave the figures recorded in the fifth column under "sum". The weight of the mixed acetone and water divided by the specific gravity at 20° gave the actual volume occupied by the mixture at that temperature. The difference between this figure and that representing the sum of the volumes of the unmixed liquids, when divided by the latter figure gave the "Per cent. of Contraction," the figure recorded in the last column.

TABLE II. VOLUME AT 20°.

Acetone. Per cent.	Water. Per cent.	Acetone. Cubic centimeter.	Water. Cubic centimeter.	Sum. Cubic centimeter.	Actual volume.	Contraction. Per cent.
95.01	4.99	50.161	2.091	52.252	51.802	0.861
90.09	9.91	47.303	4.140	51.443	50.620	1.600
87.88	12.12	42.291	4.629	46.920	46.041	1.873
80.04	19.96	40.831	8.083	48.914	47.552	2.784
75.02	24.98	38.086	10.065	48.151	46.572	3.279
70.04	29.96	35.528	12.058	47.586	45.919	3.503
60.06	39.94	30.574	16.135	46.709	44.840	4.002
50.10	49.90	25.458	20.120	45.578	43.710	4.089
40.03	59.97	20.384	24.232	44.616	42.885	3.880
30.83	69.17	15.845	28.207	44.052	42.579	3.344
19.67	80.33	10.143	32.860	43.003	41.982	2.374
10.01	89.99	5.066	36.137	41.203	40.694	1.236

The weights, recalculated in the same way but using the specific gravities of water and acetone at 25°, which are respectively 0.78630 and 0.99712, are recorded in the following table:

TABLE III. VOLUME AT 25°.

Acetone. Per cent.	Water. Per cent.	Acetone. Cubic centimeter.	Water. Cubic centimeter.	Sum. Cubic centimeter.	Actual volume.	Contraction. Per cent.
95.01	4.99	50.522	2.094	52.616	52.153	0.880
90.09	9.91	47.644	4.144	51.788	50.958	1.603
87.88	12.12	42.596	4.634	47.230	46.324	1.918
80.04	19.96	41.126	8.092	49.210	47.850	2.779
75.02	24.98	38.361	10.077	48.430	46.858	3.241
70.04	29.96	35.784	12.072	47.856	46.151	3.561
60.06	39.94	30.795	16.153	46.948	45.067	4.006
50.10	49.90	25.642	20.143	45.785	43.911	4.093
40.03	59.97	20.531	24.260	44.791	43.050	3.889
30.83	69.17	15.960	28.240	44.200	42.722	3.344
19.67	80.33	10.217	32.897	43.114	42.090	2.374
10.01	89.99	5.102	36.180	41.282	40.764	1.255

Taking the figures in Tables II and III and calculating the contractions for every five per cent. by simple interpolation the following table is obtained:

TABLE IV.

Water.	Acetone.	Contraction at 20°.	Contraction at 25°.	Water.	Acetone.	Contraction at 20°.	Contraction at 25°.
0.00	100.00	0.000	0.000	49.90	50.10	4.089	4.093
4.99	95.01	0.861	0.880	50.00	50.00	4.087	4.091
5.00	95.00	0.863	0.882	55.00	45.00	3.983	3.987
9.91	90.09	1.600	1.603	59.97	40.03	3.880	3.889
10.00	90.00	1.611	1.616	60.00	40.00	3.876	3.887
12.12	87.88	1.873	1.918	65.00	35.00	3.589	3.632
15.00	85.00	2.208	2.234	69.17	30.83	3.334	3.334
19.96	80.04	2.784	2.779	70.00	30.00	3.272	3.272
20.00	80.00	2.789	2.783	75.00	25.00	2.838	2.837
24.98	75.02	3.279	3.241	80.00	20.00	2.403	2.403
25.00	75.00	3.280	3.242	80.33	19.67	2.374	2.374
29.96	70.04	3.503	3.561	85.00	15.00	1.824	1.833
30.00	70.00	3.505	3.563	89.99	10.01	1.236	1.255
35.00	65.00	3.753	3.787	90.00	10.00	1.235	1.254
39.94	60.06	4.002	4.006	95.00	5.00	0.619	0.627
40.00	60.00	4.003	4.007	100.00	0.00	0.000	0.000
45.00	55.00	4.046	4.050	.....	....	....	....

It was originally intended to make a determination for every five per cent. increase in the amount of acetone in the mixtures, but owing to an accident, a portion of the purified acetone was lost and from seventy per cent. acetone down, the determinations were made for each ten per cent. It will be noticed by an inspection of the table that the two series of figures, those for 20° and those for 25°, do not vary materially from each other, showing that between these temperatures the contractions of mixtures of the two liquids are practically the same. The contraction appears to reach its maximum where the weights of acetone and water employed are equal, but there is no great difference between a forty per cent. mixture and one with sixty.

ON THE HYDRATION OF CALCIUM BROMIDE AND IODIDE.[1]

By Charles O. Curtman.

Received July 16, 1894.

THE official calcium bromide of the U. S. P. is intended to be substantially anhydrous, and to contain 99.7 per cent. of pure calcium bromide. Such a salt may be obtained by saturating a solution of hydrobromic acid with pure calcium carbonate, filtering, and evaporating the solution to dryness at a temperature considerably below a red heat (about 360° C.). A solid salt may at first be obtained, containing considerable water, which melts at about 80°–81° C., and in composition closely approximates the formula $CaBr_2 + 3H_2O$. This fused salt continues to lose a small amount of water, even a few degrees above that temperature, so that it is difficult to obtain a fused salt of a definite composition.

When the heat is raised to about 180°–181° C. a greater activity appears to take place in the separation of water, and if the fused mass be cooled at that point, a salt is obtained whose formula would somewhat approximate $2CaBr_2 + 5H_2O$. At a higher temperature the water separates with a kind of effervescence, leaving a spongy, anhydrous mass.

It appears to be probable that a hydration corresponding to $CaBr_2 + 3H_2O$ exists, and may be obtained by very careful fusion at 80° C., while the intermediate one, at about 180° C., may be a mere coincidence, though closely approached by two of the commercial specimens examined.

A similar behavior was observed with *calcium iodide*, made by saturation of hydriodic acid with calcium carbonate. The salt, which fuses below the temperature of boiling water, closely approaches the formula $CaI_2 + 3H_2O$, but cannot well be isolated by fusion, on account of a gradual loss of water, even below 100° C. With a rising temperature the water escapes very slowly and gradually, and towards the end with a slight effervescence, leaving a spongy, anhydrous mass. There was no

[1] Report of Research Committee B. No. 4.

appearance of any definite intermediate stage of hydration, as was observed with the bromide.

Six specimens of calcium bromide, manufactured by different firms, were obtained in the market. They all contain water, but by no means in uniform proportions, and but little calcium bromide can be found which conforms to the directions of the U. S. P. for anhydrous salt. The following is a short résumé of the analysis of the six specimens:

No. 1. (*M.*)—Dry white powder. When 1.9109 grams were heated for half an hour to 80° C., neither fusion nor loss of weight occurred. When heated till the preparation became spongy and anhydrous, it lost 0.3250 gram, corresponding to 17.007 per cent. of water, and 82.993 per cent. of calcium bromide. When titrated with silver nitrate and potassium chromate as indicator, it showed 82.98 per cent. of calcium bromide.

No. 2. (*M.* "*Dry.*")—Dry white powder. 1.032 grams were heated to 86° C. without loss of weight or fusion. When heated to perfect dryness the loss was 0.164 gram = 15.9 per cent. of water, and 84.1 per cent. of calcium bromide. Titration with silver nitrate yielded eighty-four per cent. of calcium bromide.

No. 3. (*M. C. W.*)—White granules, which melt between 80° and 81° C. When heated to 86° C. for half an hour one gram lost 0.0032 gram = 0.32 per cent. of moisture. When heated to perfect dryness, one gram lost 0.1816 gram = 18.16 per cent. of water and 81.84 per cent of calcium bromide. In titration with silver nitrate, 0.44 gram of the salt required 36.1 cc. of decinormal silver nitrate = 81.81 per cent. of calcium bromide.

This closely approaches the proportion of $2CaBr_2 + 5H_2O$, which requires 18.34 per cent. of water and 81.66 per cent. of calcium bromide.

No. 4. (*R.*)—White semi-fused lumps which melt between 80° and 81° C. When heated to dryness, 1.1036 grams lost 0.2349 gram, corresponding to 21.28 per cent. of water and 78.72 per cent. of dry substance. In titration, 0.2493 gram required 19.65 cc. of decinormal silver nitrate, corresponding to 78.6 per cent. of calcium bromide. The composition closely approaches the formula $CaBr_2 + 3H_2O$, requiring 21.27 per cent. of water.

No. 5. (*P.*)—White granules, melting below 100° C. 0.702

gram heated to dryness lost 0.1325 gram = 18.88 per cent. of water, and 81.12 per cent. of dry substance. Titration showed eighty-one per cent. of calcium bromide. (An approximation to the formula $2CaBr_2 + 5H_2O$, requiring 18.34 per cent. of water.)

No. 6. (*P. W.*)—White granules and semi-fused lumps. 1.32 grams heated to dryness lost 0.2323 gram = 17.6 per cent. of water, and 82.4 per cent. of dry substance. Titration showed eighty-two per cent. of calcium bromide.

A series of analyses of commercial specimens of calcium iodide gave similar results. The hydration in most cases made a close approach to the formula $CaI_2 + 3H_2O$, which requires 84.465 per cent. of calcium iodide, and 15.535 per cent. of water. No preparation came into my hands showing an intermediate hydration between three molecules of water and the anhydrous state.

The result of the examination is summarized as follows:

No 1. (*M. C. W.*)—White, fused lumps. Contain 84.29 per cent. of calcium iodide, and 15.71 per cent. of water.

No. 2. (*M.*)—Yellowish-brown granules. Contain 83.92 per cent. of calcium iodide, and 16.08 per cent. of water.

No. 3. (*R.*)—White fused mass. Contains 84.1 per cent. of calcium iodide, and 15.9 per cent. of water.

No. 4. (*P.*)—Yellowish-brown granules. Contain 85.37 per cent. of calcium iodide, and 14.63 per cent. of water.

No. 5. (*P. W.*)—White, fused lumps. Contain 84.3 per cent. of calcium iodide, and 15.7 per cent. of water.

Specimens 1, 3, and 5, show a trace of nitrate.

From the foregoing it is very probable that a definite hydrate of calcium iodide exists, having three molecules of water, for the deviations from such a formula in all of the commercial specimens examined are not very large.

To reach more conclusive evidence it would be necessary to obtain the salt in definite crystals. Hence, solutions of calcium bromide and calcium iodide were made in water saturated at a temperature of 80° C., also in alcohol of various degrees of dilution (for a high per cent. alcohol would most likely furnish an anhydrous product). The temperature of the atmosphere being high (30°–36° C.) artificial refrigeration had to be resorted to.

The result was rather disappointing. The alcoholic solutions remained clear for many hours. From the aqueous solutions crystals of both bromide and iodide were obtained, but of such small size that it was difficult to make out their forms. Those of the iodide were slightly larger and less deliquescent and under the microscope showed rhombic needles and prisms, somewhat rounded, so as to resemble some forms of uric acid.

But they were so difficult to separate from the solution without adhering liquid, that weighing could only be approximate, and most likely would include some liquid as well as the dry substance.

The bromide, on titration, yielded 62.3 per cent. of calcium bromide, which would approximate the formula $CaBr_2 + 6H_2O$, which requires 64.92 per cent. of calcium bromide, and 35.08 per cent. of water.

The iodide yielded 69.9 per cent. of calcium iodide; the formula $CaI_2 + 6H_2O$ would demand 73.11 per cent.

In both salts the adhering liquid would render the result somewhat uncertain, and the yield of dry substance too low.

The evidence thus far is certainly not sufficient to draw definite conclusions, but I believe that the existence of hydrates of the formula $CaBr_2 + 6H_2O$ and $CaBr_2 + 3H_2O$, as well as of the corresponding hydrates of calcium iodide, is very probable.

July 8, 1894.

A STUDY OF THE CHEMICAL BEHAVIOR OF ARSENOPYRITE.

By Thomas Montgomery Lightfoot.

Received June 23, 1894.

THE variation in the weathering of pyrite, marcasite, and pyrrhotite, so often to be observed in nature, has already furnished material for several papers on the subject. The consideration of these differences in behavior leads to the question involving the chemical difference between these and allied mineral species. The effect of the electric current on these naturally occurring sulphides and sulpharsenides has already been investigated in this laboratory, but, so far as I am aware, no series of experiments with various oxidants has been recorded. Investigations as to the effect of potassium permanganate on

pyrite,[1] marcasite,[1] and pyrrhotite have been in progress during the period occupied by the experiments described in this paper. At the suggestion, therefore, of Prof. Edgar F. Smith, I undertook the study of arsenopyrite in several directions with the results that follow.

The material used in this investigation was obtained from the dump of an abandoned mine in Maine and was purchased from a dealer. The mineral was associated with quartz, with apparently no other impurity so far as the mass was concerned. To separate this quartz the mass was crushed until it passed through a twenty-four mesh screen; it was then subjected to a rising stream of water in a U tube which floated off the quartz and mixed grains. The material remaining in the tube was found to be entirely free from quartz. The pure material was then washed with distilled water, spread on a filter paper, and dried at a gentle heat. A magnet was used to remove any particles of iron that might have entered the material from the crusher. This purified arsenopyrite was then preserved in a glass-stoppered bottle, and portions of it ground from time to time as required in an agate mortar. An estimation of the total sulphur contained in this arsenopyrite gave as the average of three determinations 19.77 per cent., almost the theoretical for the ratio of FeS_2 to $FeAs_2$ as 1 : 1.

Action of Potassium Permanganate at the Ordinary Temperature.—The first series of experiments consisted in determining the effect of potassium permanganate solutions of varying strengths on the mineral, the oxidant being allowed to act for varying periods of time and at 100° as well as at the ordinary temperature (21°–22°). The method of procedure at the ordinary temperature was the same in each case, and was as follows: Two-tenths of a gram of the finely ground mineral were introduced into a glass-stoppered bottle and fifty cc. of the permanganate solution added. The bottle and its contents were then shaken at frequent intervals to prevent the caking of the mineral against the walls of the vessel and to expose fresh surfaces to the action of the permanganate. Four strengths of solution were employed, $\frac{1}{100}$ normal, one per cent., three per cent., and five

[1] See "A Comparative Study of the Chemical Behavior of Pyrite and Marcasite," by A. P. Brown. *Proc. Amer. Philos. Soc.*, 1894.

per cent., and each was allowed to act for periods of one, two, three, four, and five hours. Duplicate trials were made in each case. After the solution had been in contact with the mineral for the specified time the contents of the bottle were thrown on a filter, the residue was washed on the filter and rejected, and the filtrate was acidified with hydrochloric acid and the sulphur oxidized, and determined as barium sulphate. In this determination trouble was experienced in obtaining complete precipitation of the sulphuric acid, even after long digestion and standing, and this may account in part for the great irregularities shown in the results of these oxidations. It should be noted that the four-hour experiments (which show notable irregularities) were performed after the completion of the rest of the series, but presumably under the same conditions.

The results of this series of oxidations are tabulated below. It will be noticed that the two results given in each case sometimes correspond closely with each other and at other times one is more than double the other. There is no reason why these results should vary in this way so far as external conditions are concerned as these duplicates were in each case made at the same time and under the same conditions. The average of the two in a number of cases would seem to be nearer the expected result. Omitting consideration of the four-hour trials, reference to which has already been made, it is seen that in each case the oxidation is practically completed at the end of the first hour, and is comparatively slight after all. The mineral is not nearly so readily affected by this oxidant as the simple iron sulphides.

(1) TABLE SHOWING THE AMOUNT OF SULPHUR OXIDIZED IN ARSENOPYRITE BY POTASSIUM PERMANGANATE AT THE ORDINARY TEMPERATURE.

Strength of permanganate solution.	One hour. Sulphur oxidized. Per cent.	One hour. Average. Per cent.	Two hours. Sulphur oxidized. Per cent.	Two hours. Average. Per cent.	Three hours. Sulphur oxidized. Per cent.	Three hours. Average. Per cent.	Four hours. Sulphur oxidized. Per cent.	Four hours. Average. Per cent.	Five hours. Sulphur oxidized. Per cent.	Five hours. Average. Per cent.
$\frac{1}{100}$ normal..	0.34	0.33	0.34	0.34	0.33	0.41	0.53	0.52	0.52	0.36
	0.33		0.34		0.49		0.51		0.27	
1 per cent...	0.25	0.42	0.31	0.28	0.38	0.39	0.73	0.74	0.25	0.35
	0.58		0.24		0.40		0.75		0.46	
3 per cent...	0.61	0.56	0.43	0.36	0.40	0.39	1.20	1.30	0.55	0.50
	0.52		0.28		0.38		1.40		0.44	
5 per cent...	0.41	0.29	0.27	0.51	0.34	0.52	0.25	0.44	0.59	0.48
	0.16		0.75		0.69		0.63		0.33	

Action of Potassium Permanganate at 100°.—In conducting experiments at 100° the bottles containing the mineral and permanganate solution were suspended in boiling water, which covered about one-half of the bottle, and the stoppers introduced after the contents of the bottle had reached the temperature of the water. The other details of these experiments were the same as for those conducted at the ordinary temperature. The action in this case was considerably more energetic, and the results obtained were much more concordant. The best results in this case were with the $\frac{1}{100}$ normal solution which are remarkably close in duplicate and the averages show a regular rise in the amount of sulphur oxidized in proportion to the time of oxidation. The one per cent. solution gave discordant results, but curiously the averages show a fairly regular rate of oxidation. The three and five per cent. solutions give concordant results in duplicate and show on the other hand an approach to the character of oxidation shown at the ordinary temperature, but several times greater in degree. The oxidation for each of the three and five per cent. solutions seems to be nearly complete at the end of the first hour, the rate of oxidation thereafter being very slow.

The results of this series of experiments are given in the following table, along with their averages:

(2) TABLE SHOWING THE AMOUNT OF SULPHUR OXIDIZED IN ARSENOPYRITE BY POTASSIUM PERMANGANATE AT 100°.

Strength of permanganate solution.	One hour.		Two hours.		Three hours.		Four hours.		Five hours.	
	Sulphur oxidized. Per cent.	Average. Per cent.	Sulphur oxidized. Per cent.	Average. Per cent.	Sulphur oxidized. Per cent.	Average. Per cent.	Sulphur oxidized. Per cent.	Average. Per cent.	Sulphur oxidized. Per cent.	Average. Per cent.
$\frac{1}{100}$ normal..	0.60	0.59	0.82	0.77	1.05	1.05	1.09	1.19	1.28	1.29
	0.57		0.71		1.06		1.30		1.31	
1 per cent...	1.06	0.67	1.44	1.13	2.27	1.25	1.25	1.27	1.46	0.85
	0.29		0.83		0.24		1.28		0.25	
3 per cent...	1.45	1.31	1.36	1.26	1.61	1.53	1.56	1.57	1.24	1.59
	1.18		1.16		1.45		1.59		1.95	
5 per cent...	1.12	1.40	1.25	1.33	1.36	1.41	1.74	1.77	1.70	1.73
	1.68		1.40		1.46		1.80		1.75	

The foregoing results will be more significant if compared with the results of similar experiments made with related minerals. As already noted, experiments on the chemical behavior of pyrite

and marcasite have been conducted in this laboratory recently, and from the average results of the action of potassium permanganate on the above two minerals I have been enabled to compile a comparative table in which they are compared with my results on arsenopyrite. In order to compare the action of the permanganate on the sulphur of these three minerals on equal terms, I have calculated from Brown's tabulated results of average amounts oxidized the percentage of the contained sulphur oxidized, and doing the same for my averages on arsenopyrite have combined these calculated percentages in a table in which the action of varying strengths of solution for varying times on the three minerals can be seen at a glance.

(3) TABLE SHOWING PERCENTAGE OF THE CONTAINED SULPHUR OXIDIZED BY POTASSIUM PERMANGANATE IN ARSENOPYRITE (A),[1] PYRITE (P),[2] AND MARCASITE (M).[2]

		Strength of Permanganate Solution.							
		$\frac{1}{100}$ normal. 22°.	One per cent. 22°.	Three per cent. 22°.	Five per cent. 22°.	$\frac{1}{100}$ normal. 100°.	One per cent. 100°.	Three per cent. 100°.	Five per cent. 100°.
One hour...	A	1.69	2.12	2.75	1.45	2.98	3.44	6.66	7.11
	P	1.46	3.20	4.78	5.19	7.59	11.31	11.74	14.91
	M	2.01	2.29	5.25	4.33	5.94	12.06	12.13	15.52
Two hours..	A	1.73	1.41	1.83	2.61	3.89	5.74	6.14	6.74
	P	2.19	2.68	4.26	5.79	8.85	13.09	12.81	14.10
	M	3.48	2.27	4.18	6.39	7.20	11.12	14.94	15.52
Three hours.	A	2.03	2.01	1.98	2.24	5.32	6.37	7.77	7.14
	P	2.59	3.49	5.25	5.19	6.29	15.71	12.77	18.47
	M	3.82	3.86	5.38	6.18	7.04	16.05	17.66	24.88
Four hours.	A	2.66	3.74	6.58	2.24	6.04	6.43	8.00	8.88
	P	3.26	3.46	4.78	5.42	(3.82)	11.46	20.12	22.24
	M	(2.34)	4.35	5.40	5.92	10.56	13.87	18.37	27.84
Five hours..	A	2.01	1.81	2.52	2.36	6.61	4.33	8.08	8.76
	P	3.22	3.37	4.78	5.66	10.57	12.90	20.77	28.09
	M	4.46	4.20	5.25	7.08	10.51	17.06	(14.16)	30.67

From the above table a plat has been made to show the rates of oxidation of sulphur in arsenopyrite by different strengths of potassium permanganate solutions acting for different times, the results obtained by each strength of solution being combined into a continuous curve (Plate I). The points already mentioned above as to the action of different strengths of solution

[1] Calculated from averages as given in Tables (1) and (2).

[2] Calculated from average results as given by Brown in "A Comparative Study of the Chemical Behavior of Pyrite and Marcasite." *Proc. Amer. Philos. Soc., 1894.*

are here graphically shown. A large value has been given the vertical component (percentage oxidized) in order to separate the curves more fully.

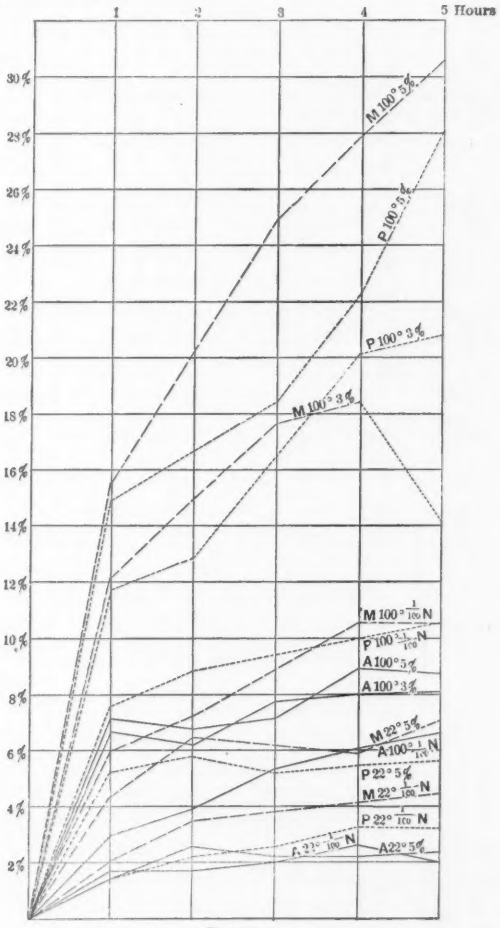

PLATE I.

A comparative plat is also given (Plate II) of selected results from table (3) in which only those curves for arsenopyrite are

selected which present a reasonable degree of regularity. They are not, however, necessarily the best in the pyrite-marcasite series.

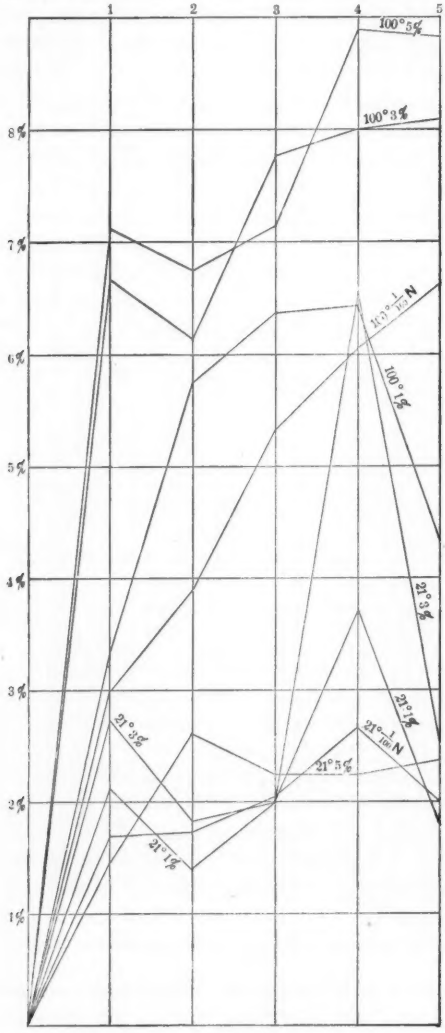

PLATE 2.

A smaller value is here given to the vertical component than in the last case in order that the pyrite and marcasite curves may be platted in full, as they rise so much higher than the arsenopyrite curves. It would be natural to suppose that the curves of arsenopyrite would be more comparable to those of marcasite than to those of pyrite on account of the isomorphism shown by their crystals, and an inspection of the platted curves will show that this is in general, correct. Take for instance the curves showing the action of $\frac{1}{100}$ normal solution of permanganate at ordinary temperature (marked A, 22°, $\frac{1}{100}$ N, etc.); it is seen that at two, three, and five hours the per cent. of oxidation of the contained sulphur in marcasite is almost exactly double that for arsenopyrite. The same condition of affairs is seen on comparing the $\frac{1}{100}$ normal solutions at 100°. It has already been noted that with the more concentrated solutions of permanganate at 100° the greater part of the oxidation of the arsenopyrite has taken place at the end of the first hour, but in the case of the pyrite and marcasite this is not the case. Their curves of oxidation rise rapidly for the three per cent. and five per cent. solutions, and are hence not comparable to those of arsenopyrite. The entire results given in table (3) are not platted here as they would simply confuse those already shown, but those obtained in the cold would serve to further illustrate the comparison that has been made between arsenopyrite and marcasite. The fact above illustrated that the sulphur in marcasite oxidizes twice as rapidly as that in arsenopyrite is what we might expect from the formula of the two minerals, marcasite being FeS_2 and arsenopyrite FeSAs.

Action of Hydrochloric Acid Gas on Arsenopyrite at Elevated Temperatures.—Experiments on the removal of sulphur from arsenopyrite by the action of hydrochloric acid gas at elevated temperatures were tried in the following manner. Two-tenths of a gram of the finely ground mineral, weighed out in a porcelain boat were subjected to the action of a stream of dry hydrochloric acid gas for one, two, and three hours at 300° and 325°, the temperatures being graded by the melting points of various salts. The sulphur in the material remaining in the boat after the action of the hydrochloric acid was determined as barium

sulphate, and the amount lost estimated by difference. While no very large amounts of sulphur were removed in this way (except in one case) the amount of arsenic driven off in the process seemed to be considerable, a large sublimate of metallic arsenic forming in the tube, and some passing out with the stream of gas. As will be seen from the results as given in the table (4) the difference in temperature between 300° and 325° caused a marked difference in the amount of sulphur removed. The temperature called 300° was between the melting points of acid sodium sulphate, $NaHSO_4$, and sodium nitrate $NaNO_3$; that called 325° was between sodium nitrate, $NaNO_3$, and potassium chlorate, $KClO_3$. The boats containing the mineral were heated in glass tubes so that the reaction could be watched. The amounts of sulphur removed at the lower temperature show no notable increase between the second and third hour, while those at the higher temperature show rapid increase of sulphur lost with the increase of time, perhaps indicating a critical temperature for the reaction of hydrochloric acid with the mineral. A comparison of these results with those obtained by Brown[1] for pyrite and marcasite is given in the table, the results being calculated to percentage of contained sulphur.

(4) TABLE SHOWING RELATIVE AMOUNTS OF SULPHUR REMOVED FROM ARSENOPYRITE, PYRITE AND MARCASITE BY ACTION OF DRY HYDROCHLORIC ACID GAS AT ELEVATED TEMPERATURES.

	One hour.		Two hours.		Three hours.	
Mineral.	Amount of sulphur removed.	Percentage of total sulphur.	Amount of sulphur removed.	Percentage of total sulphur.	Amount of sulphur removed.	Percentage of total sulphur.
Arsenopyrite, 300°	1.10	5.56	1.84	9.32	1.86	9.42
Pyrite, 300°	10.73	20.10	....	....	....	....
Marcasite, 300°	7.19	13.48	....	....	....	....
Arsenopyrite, 325°	1.62	8.29	2.82	14.29	12.21	61.78
Pyrite, 325°	....	....	....	....	17.13	32.12
Marcasite, 325°	....	....	....	....	10.70	20.06

Action of a Solution of Copper Sulphate Under Pressure on Arsenopyrite.—A single experiment on the action of copper sulphate in water solution on this mineral was tried by heating two-tenths of a gram of the finely ground mineral with a dilute solution of the salt in a sealed glass tube for six hours at a temperature approximating 200°. But little ferrous iron was found in

[1] Op. cit.

the solution, which seems to indicate that the iron present in the mineral is ferric. Some crystalline green arsenate (?) of copper was observed in the tube.

The results of the oxidation experiments detailed in this paper seem to bear out the relationship between arsenopyrite and marcasite indicated in the isomorphism of the two minerals, but the arsenic seems to be a disturbing element which fixes a limit, at an early stage of the oxidation, to further action of any given strength of the oxidant. The experiments with hydrochloric acid gas seem again to show the disturbing action of the arsenic present, which, at the higher temperature at least, is probably removed by heat alone, as is the case with the majority of diarsenides, leaving finally a compound readily acted on by the hydrochloric acid as shown by the large amount of sulphur removed in the three-hour's experiment at 325°. The results of this series of experiments are, therefore, not very significant as compared with those for pyrite and marcasite as given in Brown's paper. If, as indicated by the oxidation experiments, the arsenopyrite is rather to be compared with marcasite, in which Brown has shown that the iron is in the ferrous condition, we may look on arsenopyrite as a ferrous compound, but this conclusion seems to be negatived by the result of the single experiment of decomposing the mineral in a solution of copper sulphate under pressure. In this experiment it will be remembered, no considerable amount of ferrous iron was found. Further research in this latter direction must be made before definite statements as to the constitution of arsenopyrite can be formulated.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

THE PROTEIDS OF THE KIDNEY BEAN.[1]

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

THE only work on the proteids of the kidney bean having importance at the present time, is that of Ritthausen. This investigator in 1883, stated[2] that the extract of the white bean

[1] Reprinted from the report for 1893 of the Connecticut Agricultural Experiment Station, New Haven.

[2] *J. prakt. Chem.*, 103, 204.

which has a weak alkaline reaction, and is extremely difficult to filter, when made clear by subsidence, yields on adding acetic acid, a voluminous precipitate, amounting to about eleven per cent. of the seed, having the following composition:

Carbon	51.48
Hydrogen	7.04
Nitrogen	14.40
Sulphur	0.42
Oxygen	26.66
	100.00

In 1884, Ritthausen[1] published the results of further study of this seed. He then stated that the proteid, obtained in his earlier experiments, was wholly insoluble in five per cent. sodium chloride solution, but partially dissolved in two per cent. brine, and by diluting was precipitated in a form entirely like the original substance. By treating the bean meal with alcohol he found that clarification of the extracts was greatly facilitated and he, therefore, used meal so treated in his subsequent experiments.

By extraction with two per cent. sodium chloride solution, and clearing the extract by subsidence, he obtained, in two cases, precipitates of proteid, amounting respectively to 13.2 and 11.45 per cent. of the meal. Another preparation, equal to 8.67 per cent., he obtained from an aqueous extract of the meal precipitated with hydrochloric acid, the precipitate being redissolved in potash water and the solution neutralized after filtering clear. By extracting the bean meal with dilute hydrochloric acid, he obtained 10.07 per cent. of proteid. Preparations made by precipitating aqueous solutions with hydrochloric acid and sodium chloride extracts by dilution and submitting the precipitates to analysis without re-solution and consequent purification, had a composition similar to that found for the earlier preparations.

The precipitate obtained from hydrochloric acid solutions, had a different composition, agreeing with that of the proteid extracted by dilute salt solution both from the older preparations and from the freshly formed precipitate produced by acids in the aqueous extract, as well as with that of the insoluble portion remaining after this extraction, and also with that of the

[1] *J. prakt. Chem.*, N. Folge, 29, 452.

precipitate produced by hydrochloric acid in the aqueous extract, redissolved in dilute potash water and precipitated by neutralization. An average of five quite closely agreeing analyses of the proteid thus obtained, is shown by the following figures:

Carbon	52.55
Hydrogen	7.09
Nitrogen	16.18
Sulphur	0.43
Oxygen	23.75
	100.00

This proteid, Ritthausen remarked, "is so similar in composition to albumin, that one might be led to regard it as an albumin, low, indeed, in sulphur." In most respects the experiments of the writer now to be detailed, confirm these observations of Ritthausen, but in two particulars his statements have not been corroborated. The reaction of the aqueous extract, I have found in all cases, to be distinctly acid, even when the beans were tested within two minutes after crushing. Ritthausen's statement that his earlier preparations were wholly insoluble in five per cent. solution of sodium chloride, while a very considerable quantity was dissolved by two per cent. brine, is difficult to understand, unless as implied, though not directly so expressed, the presence of the proteid was detected by largely diluting the salt-water extracts. The writer has found that strong saline solutions, unless containing a large proportion of this proteid, are not precipitated by dilution, the salt being present in sufficient quantity to serve as a solvent for the diminishing percentage of the dissolved proteid.

I have been able to identify and obtain in a state of comparative purity, two distinct proteids, one, the most abundant, having quite the properties of a globulin, which I shall designate *phaseolin* and another, not so definite in character, that may be distinguished as *phaselin*.

Preparation of Phaseolin.

An extract was prepared by treating 500 grams of freshly ground bean meal,[1] which had been previously exhausted with ether, with one liter of two per cent. sodium chloride solution.

[1] The "White Medium Field Bean," the seeds being about ½ inch or one cm. in length, was used for this investigation.

The residue was strained out on coarse linen squeezed dry in a screw press, and again treated with a liter of the two per cent. salt solution. The resulting extract filtered very slowly and not wholly clear; about nine-tenths of it was finally obtained as a turbid filtrate. This was saturated with ammonium sulphate and the precipitate produced collected on a filter and separated as completely as possible from the solution. This precipitate was removed from the filter and treated with water. Much of the substance went into solution, but a considerable part remained undissolved. After twenty-four hours filtration, a very nearly clear liquid was obtained, amounting to about two-thirds of the solution. This was then dialyzed in a stream of river water for six days. When thus freed from chlorides, the contents of the dialyzer were transferred to a filter, but only a part of the separated proteid remained on the paper, the filtrate being milky. The precipitate collected was washed with water, alcohol and ether, and when dried over sulphuric acid, weighed sixteen grams. This preparation had the following composition:—1.

PHASEOLIN, PREPARATION 1.

	I.	II.	Average.	Ash-free.
Carbon	51.73	....	51.73	52.23
Hydrogen	6.89	....	6.89	6.95
Nitrogen	16.28	16.14	16.21	16.37
Sulphur	0.68	0.54	0.61	0.62
Oxygen	....	....	....	23.83
Ash	0.96	....	0.96	....
				100.00

As this preparation separated from a not perfectly clear solution, and therefore, presumably, was impure, a part of it was dissolved in one per cent. sodium chloride brine and precipitated by dilution. After standing a few hours to settle, the precipitate was filtered off and washed with distilled water, with alcohol and with ether. Its composition is as follows:—2.

PHASEOLIN, PREPARATION 2.

		Ash-free.
Carbon	52.35	52.60
Hydrogen	6.63	6.69
Nitrogen	16.42	16.56
Sulphur	0.63	0.63
Oxygen	....	23.52
Ash	0.82	....
		100.00

Another preparation was made by treating the fine ground beans, previously extracted both with ether and alcohol, with ten per cent. sodium chloride solution, as long as any proteid was removed. The extract was allowed to stand over night and the very nearly clear, greenish-yellow liquid was decanted from the sediment and saturated with ammonium sulphate. The precipitated proteid was collected on a filter and dissolved in dilute salt solution. This liquid was filtered as clear as possible and then dialyzed. When freed from chlorides, the globulin which had separated was filtered off, and washed and dried in the usual manner. This preparation, 3, had the following composition:

PHASEOLIN, PREPARATION 3.

	I.	II.	Average	Ash-free.
Carbon	52.19	....	52.19	52.60
Hydrogen	6.67	....	6.67	6.72
Nitrogen	16.01	16.06	16.04	16.17
Sulphur	0.63	....	0.63	0.63
Oxygen	....	....	....	23.88
Ash	0.79	....	0.79	....
				100.00

As this preparation, 3, separated from a solution which could not be filtered perfectly clear, it is undoubtedly impure. In order to determine whether the preparations thus far obtained were mixtures of two or more globulins, the following were made by fractionally precipitating the extracts. The extraction was also carried out in such a way as to afford an approximate determination of the amount of phaseolin contained in the extracts.

One hundred grams of bean meal were treated with 500 cc. of one per cent. sodium chloride solution, strained through cloth, and allowed to stand so as to deposit most of the suspended matter. The solution was then decanted and 350 cc. of nearly clear extract obtained, being, therefore, approximately seven-tenths of the whole. This solution was then diluted with 1,050 cc. of distilled water and allowed to stand until the precipitate so produced had settled. The latter was collected on a filter, washed with alcohol and ether, and when air-dried was found to weigh 4.76 grams; preparation 4. The filtrate from 4 was diluted with about an equal bulk of water and carbon dioxide was

passed through it. After standing some time, a precipitate settled out, leaving the liquid nearly clear. This was decanted and the precipitate collected on a filter and treated like 4. This gave preparation 5, which weighed 3.76 grams. The filtrate from 5 was further diluted with a considerable quantity of water and carbon dioxide again passed through the solution. This gave preparation 6, weighing, air-dry, 1.12 grams. The filtrate from 6 was treated with acetic acid, and a further small precipitate, 7, obtained, weighing 0.7 gram. The four preparations together weighed 10.34 grams, and as they were obtained from seven-tenths of the total extract, were approximately equivalent to the proteid derived from seventy grams of air-dry bean meal or to 14.77 per cent. of the meal. It is evident that in preparing the globulin by dialysis in the manner just described, only a part was obtained. As preparation 4 was separated from an unfiltered extract, it was necessary to dissolve and reprecipitate it before submitting it to analysis. It was accordingly treated with one per cent. sodium chloride solution, but had become largely insoluble in brine. The insoluble matter was filtered off, the clear filtrate diluted, and carbon dioxide passed through it as long as globulin was precipitated.

The precipitate was filtered off, washed thoroughly with water, alcohol, and ether, and dried over sulphuric acid. Only one gram of proteid, preparation 4, was recovered.

PHASEOLIN, PREPARATION 4.

	I.	II.	Average.	Ash-free.
Nitrogen	16.05	15.89	15.97	16.12
Ash	0.93	....	0.93	....

Analyses of the other preparations gave the following results:

PHASEOLIN, PREPARATION 5.

	I.	II.	Average.	Ash-free.
Carbon	52.14	....	52.14	52.54
Hydrogen	6.78	....	6.78	6.83
Nitrogen	16.35	....	16.35	16.48
Sulphur	0.62	0.53	0.58	0.58
Oxygen	....	....	....	23.57
Ash	0.77	....	0.77	....
				100.00

PHASEOLIN, PREPARATION 6.

		Ash-free.
Nitrogen	15.83	16.23
Ash	2.51	....

PHASEOLIN, PREPARATION 7.

		Ash-free.
Nitrogen	16.70	16.87
Ash	1.04	....

A larger quantity of meal was next extracted, and the extract fractionally precipitated in the following manner:

Five hundred grams of meal were treated with 1,500 cc. of one per cent. sodium chloride solution, and the extract filtered once through good filter paper. About two-thirds of the extract were thus obtained as a turbid solution. Three volumes of distilled water were added, and the large precipitate formed was designated A. Through the filtrate from A, a current of carbonic acid gas was passed, and the resulting precipitate filtered off and marked B. Precipitate A was treated with about fifty cc. of ten per cent. sodium chloride brine and filtered as well as possible. A considerable part of A had become insoluble, and the filtration was exceedingly slow. After two and one-half days, most of the solution had filtered very nearly clear. This was then diluted with about ten times its volume of water, and the precipitate thereby produced, filtered off, washed with alcohol and ether, and dried over sulphuric acid; preparation 8. The filtrate from 8 was again diluted with a large quantity of water and a second precipitate obtained in a like manner; preparation 9.

The filtrate from 9 gave a very small additional precipitate with carbon dioxide, weighing, when dry, only 0.2 gram. A portion of precipitate B was dried and marked preparation 10. Five grams of precipitate B were dissolved in one-half per cent. sodium chloride solution, previously heated to 70°, filtered hot from the considerable insoluble matter, an equal volume of water heated to 70° was added to the filtrate, and the solution very slowly cooled. The proteid separated in well-developed spheroids. When this precipitate was filtered off and washed with water, the substance began to dissolve, as the salts were washed out, in the same way as the globulins of the oat kernel, castor bean, and hemp-seed dissolve, when they are washed with water, after separating from warm salt solutions on cooling. Alcohol was then added to the contents of the funnel, and the substance washed with alcohol and ether, and dried. This preparation, 11, weighed two grams.

The insoluble proteid filtered from the solution which yielded 11, was dissolved in two-tenths per cent. potash water and after filtering, the solution was exactly neutralized with two-tenths per cent. hydrochloric acid. The precipitate, which was very readily soluble in dilute sodium chloride solution, after washing with water, alcohol and ether, and drying, weighed 0.65 gram; preparation 12.

Another portion of precipitate B weighing 3.35 grams, was treated with one-half per cent. sodium chloride brine, and heated to 70°. The insoluble matter was filtered off, washed with hot dilute salt solution, with water, alcohol and ether, and when dried formed preparation 13, weighing 1.16 gram. The dissolved proteid separated from the filtrate and washings of 13 on gradually cooling, and after washing with dilute alcohol, absolute alcohol, and ether, gave 1.54 grams of preparation 14. All were then dried at 110°, and analyzed with the following results:

PHASEOLIN, PREPARATION 8.

	I.	II.	Average.	Ash-free.
Carbon	52.31	....	52.31	52.72
Hydrogen	7.18	....	7.18	7.24
Nitrogen	16.32	16.32	16.32	16.45
Sulphur	0.67	0.66	0.67	0.67
Oxygen	....	....	....	22.92
Ash	0.80	....	0.80	....
				100.00

PHASEOLIN, PREPARATION 9.

		Ash-free.
Carbon	51.89	52.35
Hydrogen	6.83	6.89
Nitrogen	16.37	16.52
Sulphur } Oxygen }	....	24.24
Ash	0.88	....
		100.00

PHASEOLIN, PREPARATION 10.

	I.	II.	Average.	Ash-free.
Carbon	51.89	51.98	51.94	52.74
Hydrogen	6.84	6.64	6.74	6.84
Nitrogen	16.40	....	16.40	16.65
Sulphur	0.63	....	0.63	0.64
Oxygen	....	....	....	23.13
Ash	1.52	....	1.52	....
				100.00

PHASEOLIN, PREPARATION 11.

		Ash-free.
Carbon	52.34	52.49
Hydrogen	6.78	6.80
Nitrogen	16.80	16.85
Sulphur } Oxygen }	....	23.86
Ash	0.30	....
		100.00

PHASEOLIN, PREPARATION 12.

		Ash-free.
Nitrogen	16.54	16.67
Ash	0.81	....

PHASEOLIN, PREPARATION 13.

		Ash-free.
Carbon	52.76	53.06
Hydrogen	6.81	6.85
Nitrogen	16.59	16.68
Sulphur } Oxygen }	....	23.41
Ash	0.57	....
		100.00

PHASEOLIN, PREPARATION 14.

		Ash-free.
Carbon	52.12	52.49
Hydrogen	6.68	6.73
Nitrogen	16.33	16.45
Sulphur } Oxygen }	....	24.13
Ash	0.72	....
		100.00

These results show that the greater part of the proteid extracted by sodium chloride solution, consists of a single globulin, amounting at least to fifteen per cent. of the seed. The greater part of the proteid remaining in the seed after extraction with salt solution, is presumably the same globulin, possibly inclosed in the tissue of the coarsely ground seed, so that it was not reached by the salt solution, or more likely, an insoluble or "albuminate" form of this globulin, as the following experiment indicates. After complete exhaustion with ten per cent. sodium chloride brine, of the meal from which preparation 3 was obtained, the residue was extracted with two-tenths per cent.

potash water, the extract allowed to stand over night and then decanted and precipitated with hydrochloric acid, added in very slight excess. The precipitate was washed by decantation, redissolved in potash water and filtered clear. This solution was then precipitated by hydrochloric acid, and as the proteid separated imperfectly, it was treated with alcohol and ether, and filtered off. After washing with dilute alcohol, absolute alcohol and ether, it was dried and analyzed; preparation 15.

PHASEOLIN, PREPARATION 15.

		Ash-free.
Carbon	51.57	52.47
Hydrogen	6.78	6.90
Nitrogen	15.71	16.00
Sulphur } Oxygen }	....	24.63
Ash	1.72	....
		100.00

Another preparation of the globulin was made by treating 100 grams of bean meal, previously extracted with ether, with 500 cc. of *distilled water*, straining through a cloth, allowing the extract to stand over night to deposit suspended matter and decanting the slightly turbid liquid, of which the 250 cc. thus obtained were diluted to 2,000 cc. and treated with a current of carbonic acid gas. On standing, the considerable precipitate settled out so that the solution could be filtered. The precipitate was washed with water, alcohol, and ether, and when dried over sulphuric acid weighed 5.5 grams. As the extract employed, measured one-half the volume of the water applied to the meal, the yield of globulin was in this case approximately eleven per cent. of the bean meal. Although precipitated from a somewhat turbid solution, and consequently not quite pure, this preparation was analyzed with the following results:

PHASEOLIN, PREPARATION 16.

	I.	II.	Average.	Ash-free.
Carbon	52.48	52.49	52.49	53.22
Hydrogen	6.71	6.86	6.79	6.86
Nitrogen	16.32	16.18	16.25	16.48
Sulphur	0.45	0.48	0.47	0.48
Oxygen	....	....	....	22.96
Ash	1.53	1.27	1.40	....
				100.00

It is evident from this analysis that the principal proteid extracted by water, is the same as that extracted by saline solutions, and as this substance is precipitated from the aqueous extract by dilution, it is undoubtedly dissolved by aid of the salts contained in the beans. It is not probable that the acid contained in the seed causes this solution, for in that case the proteid would not be precipitated by dilution, a considerable excess of acid being necessary to effect its precipitation. The meal after extracting with water, as just described, was treated with one per cent. sodium chloride solution, the extract filtered, largely diluted with water, and charged with carbon dioxide. Only a trifling precipitate resulted which, when prepared in the usual manner, weighed 0.52 gram. This preparation, 17, ash-free, contained 16.29 per cent. of nitrogen. These results show that nearly, if not quite as much of the globulin is extracted by water with help of the salts of the seed, as by use of stronger salt solutions.

[TO BE CONTINUED.]

A NEW AUTOMATIC PIPETTE.[1]

By Emil Greiner.

WHEN taking a great number of samples in succession of the same volume of the same liquids, it is quite desirable to have a measuring instrument which will automatically take up the exact volume of liquid, without having to draw the same by mouth and watch for the mark, as is done when using the ordinary volumetric pipette. Therefore, I have devised an automatic pipette for such purposes, which is at present successfully employed in connection with the Babcock milk test. A glance at the accompanying cut will explain the practical value of this instrument, and as the pipettes can be made in all sizes required up to 50 cc., it can be adopted in many instances, where pipettes are used often and where accuracy is desired.

[1] Read before the New York Section, March 9, 1894.

NEW BOOKS.

AN ELEMENTARY MANUAL OF CHEMISTRY. BY FRANK H. STORER, AND WILLIAM B. LINDSAY, BEING A REVISION AND REWRITING OF PROFESSOR W. R. NICHOLS' ABRIDGMENT OF ELIOT AND STORER'S MANUAL. pp. 453. New York, Cincinnati, and Chicago: American Book Company. 1894. Price, $1.20

This work, which as the authors aptly put it, "is the lineal descendant of the Eliot and Storer Manual and the Nichols' Elementary Manual," will be greeted by its former acquaintances with the consideration due the scion of an ancient family. To those who knew not its antecedents, may be said, "it is not written in the interest of any particular theory or of any one system of nomenclature or of notation." Starting with the physical and chemical changes familiar to every one, the air and the water—mixture and chemical compound—the elementary substances composing them are studied and with these the elements naturally grouped with them. Following these are chapters upon theory, the non-metals, the metallic elements, and the periodic law, closing with an admirable appendix upon chemical manipulation, a subject too often neglected.

Nearly one hundred pages have been added to the abridgment, largely to the theoretical and physico-chemical parts, which in the former edition were conceded to be scantily treated, although there is scarcely a chapter of the descriptive part to which important additions have not been made. The sections upon chemical calculations, atomic and molecular weights, Avogadro's law, empirical and rational formulas are clearly and concisely written and should present little difficulty to the student.

The book is peculiar in the attention paid to organic chemistry, which one hardly expects to find in a manual of this kind, nearly one fourth of the volume being devoted to this branch. The topics of flame and combustion, isomerism and the three important "series" of organic compounds are carefully explained and illustrated, closing with a chapter upon "some carbon compounds derived from plants and animals" embracing the sugars and allied bodies, the principal alkaloids and dyes and a few

pages upon physiological chemistry. Nor have the newer methods of industrial chemistry been overlooked, as for example, the Solvay process and the bi-sulphite process of paper manufacture; a brief outline of the metallurgical treatment of all the metals which are technically important, is also a valuable addition.

Some may note the brevity of the account of the action of nitric acid upon the metals, and regret the omission of the Raoult method of the determination of the molecular weight by the lowering of the freezing point, and notice some points in which the old usage has been adhered to, as for example the Chevreul explanation of the action of soap, and the symbol of arsenious oxide given as As_2O_3.

The work, however, leaves little to be desired as a text-book of general chemistry in our higher institutions of learning and cannot fail to be of more than ordinary interest to the general reader. A. H. G.

NOTES.

THE CHEMICAL MIDWINTER FAIR CONGRESS AT SAN FRANCISCO.

The great success of the international congress held in connection with the World's Fair at Chicago, in August, 1893, was probably the stimulating cause which led the chemists of the Pacific coast to organize a similar congress in connection with the San Francisco Midwinter Fair. The committee in charge of the congress consisted of Prof. W. B. Rising, chairman, Professors E. W. Hilgard, John M. Stillman, G. M. Richardson, A. L. Lengfeld and Messrs. W. M. Searby, Alfred Ropp, Edmond O'Neill, Harry East Miller, Theodore J. Wrampelmier and E. C. Burr. The sessions of the congress were held in Golden Gate Hall, 625 Sutter street, June 7, 8 and 9, 1894.

The attendance at the meeting was most gratifying in the number of chemists, although the public, not much interested in such matters, was but sparsely represented. Unfortunately, no record was kept of those in attendance and only an estimate can be made of the total number, but this was in excess of

fifty, showing the lively interest taken by the Pacific coast chemists in the success of the meeting. Only two cismontane chemists were in attendance.

In the arrangement of the program of the congress but little attempt was made to group the topics together by subjects, but the arrangement was simply such as was thought would best fill in the time. The titles of the papers read on each day of the session follow:

THURSDAY, JUNE 7, 10 A. M.

Chairman ..... W. B. Rising

1. Introductory Remarks ..... James D. Phelan
2. "Industrial Applications of Chemistry" ..... W. B. Rising
3. "A Theory of the Dissociation of the Products of Explosives" ..... W. R. Quinan
4. "Concerning the Conversion of Mechanical Energy into Chemical Action ..... J. M. Stillman
5. "Achievements and Aims of Physical Chemistry" ..... J. R. Trevor
6. "Contraction of Aqueous Solutions of Acetone" .... Karl P. McElroy
7. "Modern Conceptions of Affinity and Valence" ..... S. W. Young
8. "Analytical Notes" ..... W. B. Rising
9. "Determination of Nickel in Nickel-Steel" ..... L. R. Lenox
10. "Limitations of the Cyanide Process" ..... C. W. Merrill
11. "Device for the Adjustment of a Balance" ..... Frank Green
12. "Methods for Standardizing Reagents used in Acidimetry and Alkalimetry" ..... C. G. Hopkins and G. C. Caldwell
13. "A Volumetric Method for the Determination of Sulphuric Acid" ..... H. H. Deubam and G. C. Caldwell

FRIDAY, JUNE 8, 10 A. M.

Chairman ..... H. W. Wiley

1. "Properties of Typical Florida Soils" ..... H. W. Wiley
2. "Hawaiian Soils and Notes on the Chemistry of Certain Hawaiian Esculents" ..... A. B. Lyons
3. "The Nitrogen Contents of Soil Humus" ..... E. W. Hilgard and M. E. Jaffa
4. "Oil Tests" ..... F. Shapely
5. "Chemical and Physical Properties of some California Vegetable Oils" ..... W. C. Blasdale
6. "Some Characteristics of California Wines" ..... W. H. Krug
7. "California and Nevada Shales and their Products" A.A. Cunningham
8. "Hydrocarbons of the Pyridin and Chinoline Series in California Petroleums and Asphalts" .. Dr. Frederick Salathe
9. "Saccharimetry in Medicine" ..... A. E. Regensberger, M. D.
10. "Kryolith and its Industrial Application" ..... Theodore Armstrong

SATURDAY, JUNE 9, 10 A. M.

Chairman ..... Geo. C. Caldwell

1. "The Analytical Properties of Iron Phosphide and Phosphate" ..... L. M. Dennis and B. S. Cushman
2. "The Preparation of Crystalline Chlorides by Means of Hydrochloric Acid Gas" ..... L. M. Dennis
3. "Parapropionic and Metapropionic Aldehyde" ..... W. R. Orndorff and Miss L. L. Balcom

4. "Determination of Alcohol in Fortified Wines"....T. J. Wrampelmier
5. "The Influence of Alum, Aluminum Hydroxide, and Aluminum Phosphate on the Digestibility of Bread"..
.....W. D. Bigelow and C. C. Hamilton
6. "Chrome Ore Industry".....H. G. Shaw
7. "The Education of the Technical Chemist".....J. M. Stillman
8. "The Teaching of Chemistry".....General Discussion

The sessions were held in the morning beginning at ten o'clock and continuing until one. After luncheon each day excursions were made in San Francisco and vicinity, to points which were of interest to chemists.

On Thursday afternoon the Pioneer White Lead and Color Works, the Golden City Chemical Works and the manufacturing establishment of Clinton E. Wonden and Co., were visited.

On the afternoon of Friday the Pacific Coast Borax Works at Alameda Point, and the chemical laboratory of the University of California at Berkeley, were the objective points. The greatest interest was manifested by the visiting chemists in the manufacture of borax. In Southern California there are immense deposits of crystallized hydrous calcium borate, the mineral known as Colmanite. This mineral is easily crushed and reduced to a fine powder in which condition it is mixed with natural sodium carbonate obtained from the alkali deserts and heated under pressure with water to cause the reaction to take place, by means of which the lime appears as a carbonate and the sodium as a biborate. The process although a simple one is quite complicated from a technical point of view, and the visitors were much interested and thoroughly entertained by the exhibition.

The new chemical laboratory of the University of California was also the object of the greatest interest and profit. This laboratory is built upon the most modern plan and combines most thoroughly, convenience for work and efficiency of ventilation. Every department of chemistry taught in the institution has a separate place in the laboratory and the desks, apparatus, storerooms and laboratories were all inspected with much pleasure.

On the afternoon of Saturday an excursion was made to the Western Sugar Refinery, formerly known as the Spreckels Sugar Refinery, which is one of the largest and most complete works of the kind in the world. The whole process of refining sugar was thoroughly explained and the building and apparatus inspected from top to bottom.

From the sugar refinery the party passed to the inspection of the Union Iron Works and the Pacific Rolling Mills. The gigantic operations of these two factories in the building of the great war ships which have been constructed and are under construction at this place, were thoroughly explained. No part of the excursion was of more interest to the chemist than this. The Union Iron Works kindly placed at the disposal of the chemists their private tug for the purpose of carrying the party from San Francisco to Potrero and return. The sail on the bay was thoroughly enjoyed by all.

On Saturday evening a delightful banquet of an informal nature was held at which forty, all I hope immortal, sat down. The festivities of the banquet were continued until a late hour.

On Monday the chemists were invited to visit the California Powder Works and the Giant Powder Co., situated near the Southern Pacific Railroad, about thirty miles from San Francisco. Not a very large number was able to accept this invitation, but those who did go were fully repaid for the trip.

There is no space here for comments on the scientific papers read, but, an inspection of the titles will show the broad scope of scientific research covered by the papers presented to the congress.

The visiting chemists received every courtesy from their San Francisco brethren, and those having the congress in charge certainly deserve the heartiest congratulations for the successful way in which they carried it to a happy conclusion.

H. W. WILEY.

ERRATUM.—Page 514, fifth line from bottom of page, for "*proof* silver, etc.," read "*pure* silver, etc."